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THE KINETICS OF THE H_2S-SO_2 REACTION IN A RECYCLE REACTOR

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "The Kinetics of the H_2S-SO_2 Reaction in a Recycle Reactor" submitted by Daniel Alexander Cormode, in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

ABSTRACT

An experimental investigation of the reaction of H_2S with SO_2 in the presence of an aluminum oxide catalyst was undertaken in a recycle reactor. The reaction was studied at 453 degrees F and 760 mm Hg pressure. Reactant concentrations of H_2S varying from 2.2 to 6.3% were investigated. The ratio of H_2S to SO_2 was maintained at 2:1 in all runs. N_2 was used as the diluent.

A side reaction in which H_2S apparently decomposes in the presence of the aluminum oxide was observed when H_2S and N_2 alone were passed through the reactor. Conversions of 0.5 to 2.0% were observed at 453 degrees F and 760 mm Hg pressure. This reaction was not further investigated.

Attempts were made to correlate the experimental rate data of the reaction of H_2S with SO_2 with nine proposed reaction mechanisms. No satisfactory agreement between any of the postulated mechanisms and the experimental data could be obtained. The experimental rates of reaction are presented in tabular form as a function of reactant concentration.

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I. INTRODUCTION

Hydrogen sulfide, recovered from the processing of sour natural gas, has assumed importance as a source of sulfur in North America and France in recent years. Canadian sulfur production from all sources has increased from essentially nil fifteen years ago to one-million long tons in 1962. It is estimated that by 1968-70, sulfur production in Canada will reach 2 to $2\frac{1}{2}$-million long tons per year. Practically all of the elemental sulfur presently produced in Canada is obtained from sour natural gas in Alberta.

The first commercial vapor phase processes for recovering sulfur from H_2S produced in coke ovens were the Claus (1) and Claus-Chance (2) methods developed in the period 1883 to 1887. Reaction (1) shows the overall chemistry of these processes:

$$3H_2S + 3/2O_2 \rightleftarrows 3H_2O + 3\,x\,S_x \qquad (1)$$

$$\Delta H_R = -51{,}400 \text{ cal/gm mole } H_2S \qquad x = 8 \qquad T = 250 \text{ degrees C}$$

The original process consisted of a single reactor in which the oxidation of H_2S with air was carried out over a bauxite or iron ore catalyst. By experience, it was found that the best yields could be obtained with an exit temperature of the gases of 500 degrees F. Since radiation provided the only method of heat removal, the reaction being highly exothermic, only two to three volumes of H_2S could be converted per volume of catalyst per hour and still obtain conversions of 80 to 90%. This tended to limit the production of sulfur by this method since very large operations were required.

The I.G. Farbenindustrie (3, 4), in 1937, developed a modification of the previous processes to circumvent the problem of heat removal. Their process divided the operation into two reaction stages, consisting basically of a waste heat boiler and a catalytic reactor. Reactions (2) and (3) give the chemistry of this split stream process.

Waste Heat Boiler

$$H_2S + 3/2O_2 \rightleftharpoons H_2O + SO_2 \qquad (2)$$

H_R = -124,100 cal/gm mole H_2S T = 250 degrees C

Catalytic Converter

$$2H_2S + SO_2 \xrightleftharpoons{Al_2O_3} 2H_2O + 3/x\ S_x \qquad (3)$$

H_R = -14,650 cal/gm mole H_2S x = 8 T = 250 degrees C

As can be seen from the above heats of reaction, 80% of the total heat is now evolved in the waste heat boiler, where heat removal is a relatively simple problem. Furthermore, the conversion in reaction (2) does not begin to decrease significantly until much higher temperatures are reached. Space velocities can be increased a hundredfold in the catalytic converter as compared to the older single-stage process. A minimum temperature of 280 degrees C, the dew point of sulfur vapor, must be maintained in the converter to prevent condensation of sulfur vapor. A sulfur condenser can be added after the catalytic converter to remove the sulfur. The remaining gases can then be passed through a second catalytic converter at a lower temperature to increase the conversion of the reaction.

The I.G. Farbenindustrie (5) also developed another process for recovering sulfur from H_2S. In this process, H_2S was partially burned with air at temperatures up to 1000 degrees C. Sulfur vapor, water vapor, and SO_2 were obtained as products with sulfur yields of 60 to 90%. The unreacted H_2S and SO_2 were then reacted in a catalytic converter according to reaction (3).

In 1944 and 1945, Mathieson Chemical Corporation commenced operations in two plants in Arkansas which used the partial combustion process for the first time in North America. Sawyer and Hadner (6) report pilot plant and operating data obtained from these operations.

Estep, McBride and West (7) published an extensive review on sulfur recovery from sour natural gases and refinery gases. A description is given of two sulfur recovery plants operated by Texas Gulf Sulphur in Wyoming and Alberta. In the Wyoming plant, H_2S is burned with air at temperatures of 2175 to 2225 degrees F. The overall reactions in the furnace are represented by the following empirical equation (4):

$$H_2S + 0.5O_2 \longrightarrow 0.75S_{gas} + 0.2H_2S + 0.1SO_2 + 0.4H_2O \qquad (4)$$

These furnace gases then enter the first catalyst chamber at 675 degrees F, emerging at 730 degrees F. A space velocity of 850 scf of gas per cubic foot of catalyst per hour was employed. The sulfur vapor was then condensed and the gases flowed through a second catalytic converter entering at 510 degrees F and leaving at 580 degrees F. The plant, including the H_2S absorption system and the sulfur recovery

section operates at an efficiency of 92%.

Some information concerning the kinetics of the heterogeneous-catalytic gas-phase reaction of H_2S with SO_2 is available. Investigators such as Taylor and Wesley (8), Udintseva and Chufarov (9), Murthy and Rao (10), and Hammar (11) have studied the kinetics of this reaction; however, only Hammar used a catalyst similar to those used in sulfur recovery plants. Hammar used an integral fixed-bed reactor for studying the reaction at 209 degrees and 227 degrees C with feed concentrations of H_2S as high as 2.5%. Since the kinetic data were limited, it was decided that further work at higher temperatures and concentrations under improved isothermal conditions would be of value.

Experimental catalytic studies are performed in integral, differential, or recycle reactors. The use of a differential reactor with this system presents difficulties in formulating synthetic feed mixtures containing sulfur vapor. The use of an integral reactor eliminates the problem of synthetic feed mixtures; however, the experiment rate data so obtained may be subject to considerable error depending upon the thermal nature of the reacting system. The recycle reactor consists of a catalyst bed through which a large portion of the product stream is recycled after mixing with the incoming fresh feed. Because of the considerably reduced conversion obtained per pass through the catalyst bed, the performance of the recycle reactor approximates that of a differential reactor. The recycle reactor seemed to be the most appropriate of the three types of flow reactors for studying the reaction between H_2S and SO_2.

The major difficulties to be anticipated in using the recycle reactor arise in maintaining the reaction temperature throughout the recirculation loop to prevent the condensation of sulfur vapor and in providing a means of recirculation. Since suitable recirculation equipment was not available, a centrifugal blower was designed and fabricated for use as the recycle pump. The experimental reactor was immersed in a fluidized-sand bed which served as a constant temperature bath.

A catalyst known as Porocel, used industrially for this reaction, was obtained from Minerals and Chemicals Philipp Corporation and was used exclusively in this work. Reaction rates at H_2S concentrations of 2.2 to 6.25% were studied with a 2 to 1 mole ratio of H_2S to SO_2 with N_2 serving as the diluent. The reaction temperature was maintained at 453 degrees F by the fluidized bed. The pressure in the reactor was maintained at 760 mm Hg.

II. LITERATURE SURVEY AND THEORY

A. Reaction of Hydrogen Sulfide with Sulfur Dioxide

The reaction rate of H_2S with SO_2 in the homogeneous gas phase has been observed to be very slow; however, in the presence of a solid catalyst or water, the rate was found to be greatly accelerated. The following survey reviews the studies which have been done on the reaction in the presence of a solid catalyst.

Cluzel (12) noted that reaction between H_2S and SO_2 would not occur if these gases were first dried over calcium chloride (no other details or conditions are available). Taylor and Wesley (8) observed that most of the previous investigators (8) of this reaction had allowed water to condense in their reacting system or in their sampling system. As a result, they were in fact observing the reaction of H_2S with SO_2 dissolved in water and not the heterogeneous catalytic solid reaction or the homogeneous gas phase reaction. Taylor and Wesley studied the rate of reaction of H_2S with SO_2 in Pyrex tubes at temperatures between 370 degrees and 730 degrees C. They observed that the reaction rate was proportional to the surface area of the reaction tubes, thus indicating that the glass surface serves as a heterogeneous catalyst for this reaction. Their work showed that the rate of reaction varied directly with the partial pressure of sulfur dioxide and with the hydrogen sulfide partial pressure to the one and one-half power.

Udintseva and Chufarov (9) studied the reaction rate between 250 degrees and 300 degrees C in a glass vessel whose walls had been coated with various substances. They found that glass, aluminum and aluminum oxide were effective catalysts for the reaction.

Doumani et al (13) found that highly purified and specially treated aluminas gave complete conversion at temperatures less than 200 degrees C and at space velocities of 550 to 650 scf of H_2S per ft^3 of catalyst per hour. Bauxite and precipitated aluminas did not give complete conversions under similar conditions.

Murthy and Rao (10) used a batch recycle reactor to study this reaction at roughly 10 cm Hg pressure. The reaction was carried out at 25 degrees C so that the sulfur vapor condensed and, in addition, a hygrostat was used to maintain a constant pressure of water in the system. The overall reaction is described by equation (5):

$$2H_2S_g + SO_{2g} \longrightarrow 3S_s + 2H_2O_l \qquad (5)$$

The course of the reaction was followed by observing the decrease in pressure with time. The equipment was of glass construction with the gas mixture being circulated by a magnetically activated piston. By varying the controlled partial pressure of water vapor with the same catalysts, it was shown that water exerts an autocatalytic effect on the reaction. Adsorption weight measurement studies with the catalyst and the individual gases indicated that the adsorption of SO_2 was increased by the presence of water, while the influence on H_2S adsorption was less pronounced. The overall reaction was found to be of second order with the rate being proportional to the partial

pressures of H_2S and SO_2 each to the first power. Silver sulfide, cobalt thiomolybdate, cobalt sulfide, and molybdenum sulfide were tested as catalysts and cobalt thiomolybdate was found to be the most active.

Gamson and Elkins (14) studied the effect of space velocity on conversion at conversions approaching the equilibrium level on a Porocel catalyst in a fixed-bed reactor at temperatures of 230 degrees, 260 degrees and 300 degrees C. Hammar (11) also used an integral reactor to study the reaction over an activated alumina catalyst (cobalt and molybdenum had been added in the preparation of the alumina) at temperatures of 209 degrees and 227 degrees C. Various rate expressions were postulated and checked wwith the experimental results. The best agreement was obtained with an equation based upon an assumed mechanism of reaction between molecular sulfur dioxide and dissociated hydrogen sulfide both in the adsorbed state.

B. Adsorption of Hydrogen Sulfide

The adsorption of H_2S on γ-alumina from H_2S-H_2 mixtures between 260 degrees and 560 degrees C was studied by DeRosset et al (15). They found some evidence to support the view that when H_2S adsorbed on γ-alumina, Al-S bonds were formed. A Tamele Lewis-acid model was postulated with H_2S or H_2O being initially adsorbed on dry alumina by similar mechanisms followed by electron transfer from the sulfur or oxygen to an incompletely co-ordinated aluminum ion. The initial heat of adsorption of H_2S compared to the initial heat of adsorption of H_2O gave a ratio of 0.28, which is comparable to the ratio of the

heats of formation of Al_2S_3 to γ-Al_2O_3, which is 0.32. This hypothesis of Al-S and Al-O bond formation by chemisorption is in agreement with the thermochemistry of these bulk compounds. The adsorption of H_2S was found to be ideal, that is, independent of coverage. The postulated mechanism of Hammar, the dissociation of H_2S in the reaction of H_2S with SO_2 in the presence of an alumina catalyst, is in agreement with this work.

C. Other Reactions

(i) Dissociation of Hydrogen Sulfide

Kelley (16) has given free energy data for the reaction of H_2 with S_2 to form H_2S. Equation (6) illustrates the overall reaction.

$$2H_{2(g)} + S_{2(g)} \rightleftharpoons 2H_2S \qquad (6)$$

At 500 degrees K, $K = 3.90 \times 10^{13}$ (6)

Therefore, it would be expected that the reaction will go to completion.

Norrish and Rideal (17) investigated the kinetics of the reaction of H_2 with sulfur vapor to form H_2S. They found that the combination occurs via two means, a gas-phase reaction and a surface reaction, with both mechanisms occurring at very low rates and with the latter being more important below 285 degrees C.

Darwent and Roberts (18) studied the thermal decomposition of hydrogen sulfide and found that the thermal decomposition proceeded by homogeneous and heterogeneous reactions. The rate of the thermal reaction at temperatures less than 500 degrees C was strongly dependent upon the nature of the surface. They found the energy of activation to be 25 Kcal/mole for the heterogeneous reaction on a glass surface.

(ii) Reaction of Sulfur Dioxide with Hydrogen

Doumani et al (13) give the following reactions and equilibrium constants:

$$2SO_2(g) + 4H_2(g) \rightleftharpoons S_2(g) + 4H_2O(g) \qquad (7)$$

at 250 degrees C, $K = 6.8 \times 10^{30}$

$$SO_2(g) + 3H_2(g) \rightleftharpoons H_2S(g) + 2H_2O(g) \qquad (8)$$

at 250 degrees C, $K = 1.9 \times 10^{18}$

They also observed that H_2 and SO_2 do not significantly react at temperatures less than 325 degrees C in the presence of an alumina oxide with a high iron content.

D. Methods of Chemical Analysis

Previous investigators of the reaction of H_2S with SO_2 have used a variety of analytic methods to establish the extent of the reaction. These investigators have been largely concerned with measuring the unreacted H_2S or SO_2 or alternatively the amount of water formed.

Taylor and Wesley (8) condensed the sulfur vapor from their product gas mixture and then completely absorbed the remaining gases (H_2S, SO_2 and H_2O) in a 30% sodium hydroxide solution. The amount of reaction was then determined by weighing the absorption tube and using a material balance.

Murthy and Rao (10) followed the course of reaction by noting the change in pressure with time in their batch system. Since in their operation, the sulfur formed was condensed and the H_2O pressure was held at a constant value by a hygrostat, there was a significant decrease

in pressure. At the end of the run, dry hydrogen was pumped through their reactor and then the gases were absorbed by contacting a 30% sodium hydroxide solution. The sodium sulfite and sodium sulfide which were formed were determined by the method of Kurtenacker and Wollack (10).

Doumani et al (13) determined H_2S and SO_2 by bubbling a known volume of their gas product stream through a given volume of standard iodine solution. The excess iodine was determined by titration with sodium thiosulfate and a blank correction was obtained by bubbling a volume of air equal to the inerts in the product stream through the same volume of iodine. From this, the total amount of H_2S and SO_2 was determined. The SO_2 was then determined by titrating with sodium hydroxide the H_2SO_4 formed in the oxidation of the SO_2 by iodine.

Gamson and Elkins (14) absorbed their product gas mixture in concentrated ammonium hydroxide. The total amount of sulfur-bearing gases was determined by an iodine titration of an aliquot of sample. The H_2S was then determined in another aliquot by precipitating the H_2S as Ag_2S with $AgNO_3$ and then determining the excess $AgNO_3$ by titrating with potassium thiocyanate.

Smith (19) used the following analytical method. Pulverized pumice was boiled in cupric sulfate solution and then dried; this material was then packed into an adsorption tube. The H_2S was adsorbed on this material and could be determined gravimetrically. The SO_2 was subsequently absorbed in a H_2O_2 solution and the sulfuric acid

which was formed was determined by titration with sodium hydroxide.

Lombardo (20) published a critical review of the analytical methods for H_2SO_4 and SO_2 determinations. He concluded that the hydrogen peroxide method would be a satisfactory method of analysis. He also noted that H_2O_2 has a very high absorption efficiency for CO_2.

Kolthoff and Elving (21) describe the equipment and procedure for determing SO_2 with H_2O_2 and also state that H_2S does not interfere with the determination.

Altieri (22) describes a method for determining H_2S in air in the presence of SO_2. Ammoniacal $CdCl_2$ was used as the H_2S absorbent solution. After absorbing the H_2S, he states that it is necessary to pass pure air through the solution for a period of time, probably to remove dissolved SO_2. The resulting CdS is acidified with HCl and the H_2S is titrated with I_2 solution to a starch endpoint. He suggests that SO_2 can be determined by other absorbers in series containing H_2O_2 or I_2 solutions.

Hammar (11) in the majority of his work, determined water gravimetrically by adsorption on Dehydrite. For a limited number of runs, he also included analyses for SO_2 and H_2S. Sulfur dioxide was determined by the hydrogen peroxide method and H_2S was found by absorption in ammoniacal cadmium acetate solution. The CdS which was formed was acidified with HCl to release H_2S, which was then titrated with iodine to a starch endpoint.

Hammar experimentally proved that H_2S did not interfere with the determination of SO_2 by the H_2O_2 method. Slightly better results were obtained if the H_2O_2 solution were first acidified with some HCl whose amount was later deducted from the NaOH titration for H_2SO_4. He did not verify whether absorbing the SO_2 in the H_2O_2 and then the H_2S in ammoniacal cadmium acetate had any effect on the determination of H_2S.

Hydrogen sulfide in H_2O_2 solution in the presence of H_2SO_4 may possibly react by reactions (9) and (10).

$$H_2SO_4 + H_2S \longrightarrow S + SO_2 + 2H_2O \qquad (9)$$

$$H_2O_2 + H_2S \longrightarrow S + 2H_2O \qquad (10)$$

Although reaction (9) consumes H_2SO_4, the SO_2 formed will be converted back into H_2SO_4 by the H_2O_2. A method of checking whether the H_2O_2 absorber affects the determination of H_2S would be to first determine H_2S using an absorption train with no H_2O_2 absorber, then H_2S could be passed through both absorbers in series and the results compared to the results obtained in the earlier case.

E. Applications of the Recycle Reactor

The study of heterogeneous catalytic gas reactions is not always completely satisfactory in integral or differential fixed bed catalytic reactors. The data obtained from an integral reactor may be subject to large temperature and concentration gradients and the data must also be processed to yield rate information by some technique of differentiation. Extremely high analytic precision is required when using a differential reactor because only small changes

in concentration are involved. The differential reactor also requires the formulation of synthetic feed mixtures corresponding to various conversion levels which may be difficult to do in certain cases.

As an alternative approach, Dohse (23) in 1929 proposed the recycling of a portion of the product stream from an integral reactor. Upon mixing the recycled stream with the incoming feed stream at high ratios of recycle to feed, this reactor would assume the characteristics of a differential reactor. Such a reactor possesses the following advantages:

(a) Rate data may be obtained directly.

(b) Temperature and concentration gradients are kept to a minimum.

(c) It is not necessary to make a synthetic feed stream.

(d) The accuracy of analysis is considerably improved because of the significant difference in composition between the feed and product streams.

A considerable number of workers have used recycle reactors in various kinetic studies. These workers include Perkins and Rase (24) who studied the hydrogenation of propylene on a nickel catalyst. They studied the reaction between 110 degrees to 190 degrees F and used recycle ratios of 10 to 15.

Leinroth and Sherwood (25) investigated the hydrogenation of ethylene in a semi-batch recycle reactor at temperatures between 50 degrees to 70 degrees C. In a semi-batch reactor, the recycle reactor is first started in continuous operation with constant feed and withdrawal rates at a constant pressure. The feed and

effluent streams are then quickly shut off and one reactant component is fed at such a rate to keep the pressure constant.

Butt et al (26) studied the dehydration of ethanol and diethyl ether over alumina at 274 degrees, 294 degrees and 314 degrees C. A batch recycle system was used with pressure in the reacting system not being constant. Korbach and Stewart (27) investigated the hydrogenation of benzene in a batch recycle reactor at temperatures of 500 degrees to 600 degrees F. Constant pressure was maintained by adjusting the volume of this system. Sidorov et al (28) used a recycle reactor for investigating the ammonia synthesis reaction at 300 atmospheres and 450 degrees C.

The use of recycle reactors has been limited because of the difficulties in obtaining recirculation means capable of operating at various reaction temperatures and pressures and circulating the desired amounts.

Perkins and Rase (24) built a diaphragm pump using a neoprene diaphragm. The pump was used at temperatures between 110 degrees and 190 degrees F and one atmosphere pressure. Butt et al (26) used a Vanton flexi-liner pump with a silicone rubber liner at temperatures of 274 degrees, 294 degrees and 314 degrees C and approximately one atmosphere pressure. A centrifugal blower was used in the Leinroth and Sherwood (25) studies between 50 degrees to 70 degrees C. Their recirculating gas stream was cooled before it entered the blower and reheated afterwards. Korbach and Stewart (27) used a stainless steel

diaphragm pump in their work. The pump was operated at 400 degrees F while the reaction was carried out between 500 degrees to 600 degrees F. Korneichuk (29) outlines two means of circulating fluids: use of a piston agitator or a piston circulating pump, both of which were made of glass. Sidorov et al. (28) used what is termed a thermosyphon for recirculating a gas mixture at 300 atmospheres and 450 degrees C. The thermosyphon consists of a vertical tube whose top end was cooled and the bottom end was heated. The gas mixture flowed downward through the thermosyphon, as a result of the difference in density, out through the bottom of the reactor, and then back to the top of the thermosyphon.

Temkin (30) outlined the work which has been done in the USSR using recycle reactors and discusses their utility and application. Pozzi (31) made a comparative study of the types of reactors used for experimental kinetic investigations. By estimating the fluid flow and heat transfer properties of each by generalized correlations, he concluded that only a differential fluidized-bed or a recycle reactor could give meaningful kinetic data.

F. Theory of the Recycle Reactor

Levenspiel (32) discusses the application of the recycle reactor to the measurement of experimental kinetic rate data. A schematic diagram of a recycle reactor is shown in Figure 1.

The following nomenclature will be used in discussing the recycle reactor analysis for the reaction A --> products.

F_{Ao} = feed rate of A gm moles/hr

R_A = recycle rate of A gm moles/hr

X_{Ao} = fractional conversion of A in feed stream to product

X_{Ai} = fractional conversion of A in the stream to the catalyst bed to product

X_{Af} = fractional conversion of A in product stream to product

r_A = reaction rate of A $\frac{\text{gm-moles reacted}}{\text{hour-cc of catalyst}}$

$(r_A)_{ave}$ = reaction rate of A at some average composition

dV = differential volume of catalyst bed cubic centimeters

dX_A = differential fractional conversion of A to product

V = volume of catalyst bed cubic centimeters

ΔV = volume of catalyst bed in differential reactor

First, consider the reactor performance as if it were an integral type. In this case, the recycle stream, R = 0, and the fractional conversion of A in the feed is the same as that in the stream to the catalyst bed, $X_{Ai} = X_{Ao}$. A material balance on a differential thickness of catalyst bed for component A under isothermal steady-state reaction conditions gives:

$$- r_A \, dV = F_{Ao} \, dX_A \qquad (11)$$

As an approximation to equation (11), one may write for a differential reactor:

$$(- r_A)_{ave} \simeq \frac{X_{Af} - X_{Ai}}{\Delta V / F_{Ao}} \qquad (12)$$

Now, if the recycle of A at the rate, R_A, is introduced, equation (12) becomes for the recycle reactor:

$$(-r_A)_{ave} = \frac{X_{Af} - X_{Ai}}{V/(R_A + F_{Ao})} \tag{13}$$

Consider a material balance of A about the entire recycle reactor (between the streams entering and leaving the reactor system and the reactor itself):

$$F_{Ao}(X_{Af} - X_{Ao}) = (R_A + F_{Ao})(X_{Af} - X_{Ai}) \tag{14}$$

Substituting (14) into (13) gives:

$$(-r_A)_{ave} = \frac{X_{Af} - X_{Ao}}{V/F_{Ao}} \tag{15}$$

If $R_A \gg F_{Ao}$, then $X_{Af} \longrightarrow X_{Ai}$, with the result that:

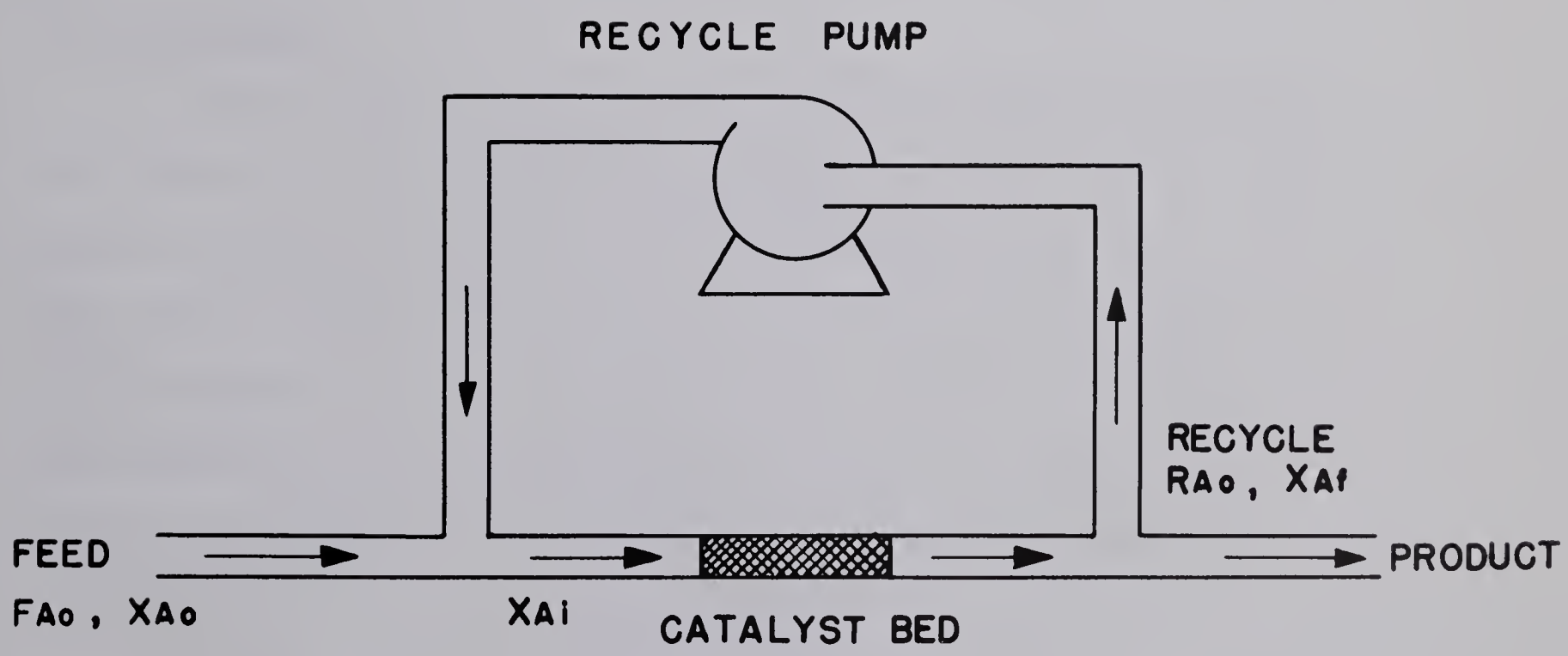
$$(-r_A)_{ave} \longrightarrow (-r_A)_{X_{Af}}$$

For the recycle reactor, one then obtains:

$$(-r_A)_{X_{Af}} \simeq \frac{X_{Af} - X_{Ao}}{V/F_{Ao}} \tag{16}$$

FIGURE 1

SCHEMATIC RECYCLE REACTOR



III. EXPERIMENTAL

A. Equipment

The equipment used in this investigation can be divided into seven sections as follows:

(i) feed system

(ii) reactor

(iii) recirculation pump and recirculation lines

(iv) air preheater

(v) fluidized bed

(vi) product system

(vii) temperature measuring system

A schematic diagram of the equipment layout is shown in Figure 2. The following sections will describe each of the seven units in detail.

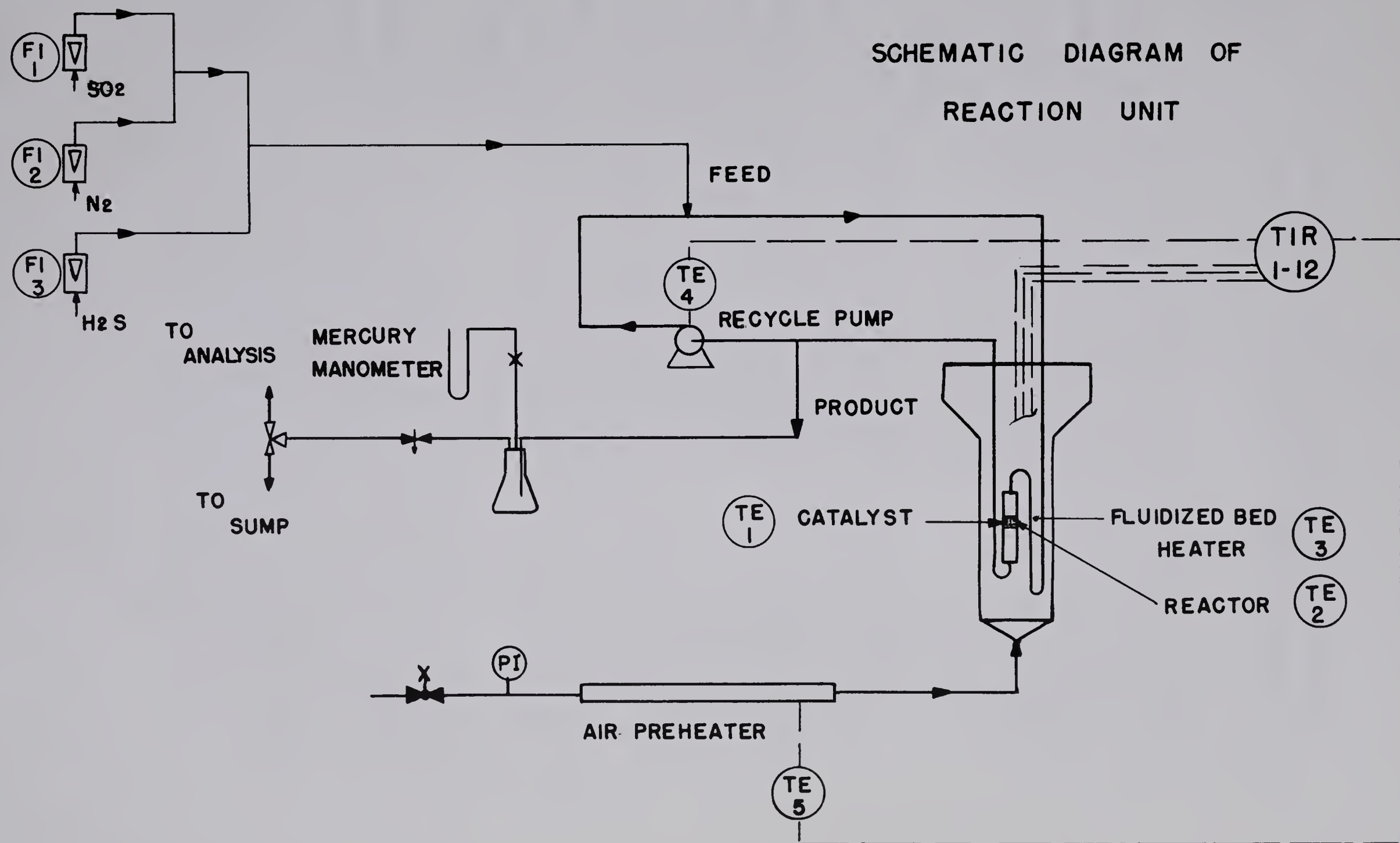
(i) Feed System

The N_2, H_2S and SO_2 were supplied by the Matheson Company and were used as received. Matheson regulators were used for reducing the cylinder pressures of the H_2S and SO_2 to the metering pressures. Surge tanks of 500 cc capacity were provided between the regulators and the rotameters in the case of H_2S and SO_2. Matheson rotameters were used to regulate the flow of each of the gases by throttling on the downstream side. The following sizes of rotameters were used:

	Catalogue No.
SO_2	601
H_2S	602
N_2	603

FIGURE 2

SCHEMATIC DIAGRAM OF REACTION UNIT



A wet-test meter was used to calibrate the N_2 rotameter. The other two rotameters were calibrated by chemical analysis of the flowing streams.

Stainless steel tubing and fittings were used in contact with H_2S, otherwise brass and copper fittings were used. The combined feed stream discharged from a 1/4 inch Type 316 stainless steel tubing into the 1/2 inch recirculation line. The 1/4 inch tubing was welded onto the 1/2 inch tubing.

(ii) Reactor

The reactor consisted of a 6 inch length of 1/2 inch nominal 316 stainless steel pipe threaded at both ends. Swagelok fittings were used to connect the reactor to the 1/2 inch stainless steel tubing which served as recirculation lines. An anti-seize compound (Silver Goop made by Swagelok) was applied to the threads to facilitate separation after they had been subjected to heating A stainless steel 200 mesh screen was mounted in the reactor to hold the catalyst in position. The gas flowed downwards through the catalyst bed.

A hole in the screen permitted the insertion (upwards into the catalyst bed) of a 1/16 inch diameter stainless steel shielded iron-constantan Thermoelectric thermocouple. A pressure seal around the thermocouple lead provided a gas tight connection through the wall of the reactor. Another thermocouple of the same type was welded at the same elevation to the outer surface of the reactor.

(iii) Recirculation Pump and Lines

Because a suitable pump could not be purchased, it was necessary to design and construct a pump in the Chemical and Petroleum Engineering Shop at the University of Alberta. Tests showed that at speeds of 6000 rpm or greater air could be circulated at the required volumetric rates using a single bladed centrifugal pump.

A pump body of mild steel was used and it proved to be satisfactory. Corrosion from the reaction system gases was not excessive because water was only present in the vapour phase. A ring of Teflon provided a seal between the pump casing and cover. The pump inlet was made by press-fitting a thick-walled hollow cylinder of stainless steel into a hole drilled in the cover. The outlet was drilled tangentially into the casing. Another hollow piece of stainless steel was press-fitted into the outlet. The sections of stainless steel serving as the inlet and outlet were threaded so that Swagelok fittings could be used to connect the pump to the recirculation lines.

The pump impeller was a straight piece of mild steel approximately 6 x 3/8 inches mounted on a 3/8 inch shaft. A support for the two bearings on the shaft was bolted to the pump casing. They were held in place by a housing which could easily be removed for lubrication, replacement of the bearings, or replacement of the packing. The seal on the shaft was provided by a graphite impregnated asbestos packing to which a further amount of aerosol graphite had been applied. An adjusting nut was used to tighten the packing when necessary to effect a seal.

The shaft was connected by a flexible coupling to a Boston Optimont gear. This gear, although normally used as a speed reducer, was used to increase the speed. The gear had a ratio of 4.06:1 and was coupled to a 1725 rpm three phase 3/4 hp Westinghouse motor giving an impeller speed of roughly 7000 rpm. A No. 30 oil with molybdenum disulfide additive (Molyslip) was used as a lubricant because it did not foam at high speeds. The gear, motor and pump were mounted on a rigid steel frame to keep them properly aligned.

Because of the mass of the pump, it was necessary to supply heat to it to make up for large heat losses by conduction. The pump was covered first with woven asbestos cloth. A 20 ohm heater was made by weaving 20 gauge Nichrome wire through another piece of asbestos cloth. This was then slipped over the pump and covered with more asbestos cloth. The heat input was regulated by a 110 volt 1 KVA variable transformer. The pump was thermally insulated from the metal frame as it was mounted on a piece of transite. A hole was drilled in the pump casing for a thermocouple well. The temperature of the pump was measured using an iron-constantan thermocouple.

Flow tests conducted on the pump showed that when the flowmeter was connected directly to the pump, it was capable of pumping at the rate of 3.6 ft^3/min at 75 degrees F and 700 mm Hg. When the pump outlet was connected to the recirculation system and this in turn connected to the flowmeter, a flow of 0.6 ft^3/min was obtained. No measurement of pump capacity at operating temperatures was obtained.

As previously mentioned, the outlet and inlet of the pump were connected to the 1/2 inch stainless steel tubing recirculation lines. The external recirculation lines connecting the pump to those in the fluidized bed were covered with asbestos cloth and then heat traced with 20 gauge Nichrome wire. This heater was connected in series with another heater on the outlet product line. A 110 volt 0.345 KVA variable transformer was used to regulate the heat to the 35 ohm heaters. The external recirculation lines were connected to those in the fluidized bed by Swagelok bulkhead fittings. The recirculation line inside the fluidized bed connecting the pump outlet to the reactor inlet had two 360 degree bends in it. It extended down into the fluidized bed, came back up, and then down, so that the gases would flow down through the catalyst bed.

(iv) Air Preheater

The air used for fluidizing the sand bed was obtained from the main air supply at 80 psig. It was passed through a Webster filter to remove any entrained oil or water. A globe valve was placed in the line before the filter to facilitate its removal for cleaning. A globe valve downstream of the filter regulated the flow of air. A pressure gauge was installed after this control valve. The air then passed through a three-foot section of one-inch mild steel pipe packed with 3/8 inch ceramic saddles. The packing was held in position by porous bronze disks. On the outside of the pipe, a layer of asbestos cloth was wrapped and 20 gauge Nichrome wire of 30 ohms resistance was wound over the asbestos. Asbestos paste was applied over the wire for

insulation purposes. Fibreglass insulation covered this and the piping connecting the preheater to the fluidized bed. A 110 volt 1 KW variable transformer was used to control the heat input.

(v) Fluidized Bed

The air coming from the air preheater passed through a conical enlarging section going from 1 inch to 5 inches in diameter. A porous bronze disk was inserted between the top of the enlarging section and the bottom flange of the fluidized bed. The disk supported the sand in the 2 feet long, 5 inch diameter fluidized bed section. The outer shell of this section was made of mild steel with a stainless steel liner to reduce corrosion by abrasion of the oxide film. This section was then enlarged at a 45 degree angle into a 10 inch diameter calming section 4 inches long. A mild steel flange was welded to the top of the calming section so that a lid could be bolted. The inlet and outlet for the recirculation lines passed through the lid by means of Swagelok stainless steel bulkhead fittings in the lid. The air finally went up a 1 inch diameter pipe to a cyclone, in which any entrained sand was removed. Heat was supplied by a 20 ohm heater which consisted of 14 gauge Nichrome wire wrapped around the section containing the sand bed. Asbestos paper served as the electrical insulation between the wire and the wall of the fluidized bed vessel. Saurereisen cement was applied over the wire to hold it in place and to serve as insulation. A layer of fibreglass and one of thermobestos insulation then followed. The heat input was regulated by

means of a 208 volt 1.6 KVA variable transformer. The temperature in the bed near the reactor was measured by means of a 1/8 inch stainless steel shielded iron-constantan, Thermoelectric thermocouple. This thermocouple along with those from the reactor were protected from the sand by a copper tube extending downwards from the lid so that only a small portion of each thermocouple was exposed. Ottawa sand of -20/30 mesh size was used in the bed.

(vi) Product System

Product gases escaped through 1/4 inch stainless steel tubing so welded that it projected partially into the external recirculation line before the pump. This 1/4 inch line was heat traced similar to that on the external recirculation lines and the heater was connected in series with them. The 1/4 inch tubing discharged into an Erlenmeyer flask, packed with glass wool.

This flask served as a trap for condensed sulfur vapor but was hot enough so that water vapor did not condense in it. A line connected the flask to a mercury manometer so that the pressure in the flask could be read. The outlet from the flask, 1/4 inch stainless steel tubing went to a Matheson needle valve and then to a two-way stopcock.

The needle valve was used to regulate the pressure in the reacting system at 14.7 psia taking into account ambient barometric pressures and varying pressure drop with changing flow rates. The two-way stopcock allowed the flow to be diverted to a sump or to the

absorption train.

The sump consisted of a flask containing water followed by a NaOH solution scrubber. By varying this level of the water in the flask, the pressure drop in this leg could be made equal to that in the analytic leg. A major portion of the H_2S reacted with the SO_2 in the water. The remaining H_2S and SO_2 was absorbed by bubbling through NaOH solution.

The absorption train consisted of three bottles in series. For runs 8 to 13, a wet-test meter was connected after the absorption train to measure the flow of N_2. The first absorber contained acidified hydrogen peroxide and the second and third absorbers contained neutral cadmium acetate. In the first bottle, a fritted glass dispersion tube was used while in the last two bottles, impinger type tubes were used. The bottles had a graduated mark on them to which they were filled each time.

In the course of the work, a wet-test meter was added to the analytic equipment train because the seal around the impeller shaft began to leak. Because of the positioning of the inlet and outlet lines on the recirculation lines, a leak at the pump is of the same composition as the gas stream being withdrawn for analysis. The existence of a leak merely meant that the total stream was not being sampled. An inert component such as nitrogen must be measured to determine the portion of the stream being sampled. Then knowing the fraction of the stream being sampled, the total amount of unreacted SO_2 can be determined.

(vii) Temperature Measurement System

The temperatures measured in the system were recorded by a Leeds Northrup, twelve point variable range, variable zero potentiometer recorder. Double readings were taken of each of the temperatures measured in the system. On the remaining two junctions, a Leeds Northrup K2 potentiometer was connected for the purpose of calibrating the recorder scale and daily checking the calibration. The stainless steel shielded thermocouples were calibrated against a thermometer at 500 degrees F and were correct within ± 0.25 degrees C. After the installation of two of the thermocouples in the reactor, it was found that they indicated the same temperature as the thermocouple in the sand bed when the reaction unit was at thermal equilibrium at room temperature.

B. Materials

The Matheson Company specified the following minimum purity limits on the gases supplied:

N_2	99.996%	(prepurified grade)
SO_2	99.98%	(anhydrous grade)
H_2S	99.5%	(C.P. grade)

These gases were used directly without further purification.

The catalyst used in this investigation was donated by Minerals and Chemicals Philipp Corporation. The properties of the catalyst were given on a data sheet (33) supplied by the company.

Porocel Sulfur Recovery Catalyst

1.	Volatile Material		6%
2.	Chemical Composition	Al_2O_3	89.0%
	(Volatile-free basis)	Fe_2O_3	5.0%
		TiO_2	2.8%
		SiO_2	2.6%
		Insoluble	.6%
3.	Density	$\approx$ 55 lb/ft^3	
4.	Surface area	215 m^2/gm	

Before using the catalyst, a sample of -20 to +30 mesh size was dried at 500 degrees F for 24 hours and then placed in a glass-stoppered bottle. Portions of this prepared catalyst were used as the catalyst charges for the reactor.

C. Procedures

(i) Operation of Equipment

Approximately two hours were required to achieve thermal equilibrium in the system at a temperature of 450 degrees F after startup with the fluidized bed heater and air preheater previously turned off. To reduce startup time, these two heaters were generally left on along with the air for fluidizing, thus requiring only the pump and external recirculation line heaters to be turned on. In practise, the catalyst bed temperature should be a function of the rate of heat removal from the bed and the rate of heat generation in the bed. The latter was different for each run and so, to achieve a constant catalyst bed temperature, it was necessary to select a

fluidized bed temperature a few degrees cooler than 454 degrees F and then check the temperature of the catalyst bed with the reaction being conducted. Minor temperature adjustments could then be made.

The N_2 flow was set on the rotameter and the back pressure in the sulfur trap was noted when the N_2 was flowing to the sump. This flow was then diverted to the analytic absorption train with the bottles filled with water and the back pressure was noted. The water level in the flask in the line going to the sump was adjusted so that the back pressures were equal for the two alternative flow paths.

A flow of one component was selected and the amount of the other component was then calculated on the basis of the ratio of 2 moles of H_2S per mole of SO_2. The rotameter readings of these components were then found from the calibration curves. The desired rotameter readings were then set with the flow being directed to the sump. The recycle pump was started and the catalyst bed temperature was checked and a correction in the fluidized bed temperature was made if necessary. The barometric pressure was noted and the required back pressure in the sulfur trap to give a pressure of 760 mm Hg at that point was calculated. This pressure was then set in the sulfur trap by means of the Matheson needle valve.

The H_2O_2 absorber solution consisted of 10 cc of 30% H_2O_2 in 250 cc of water with methyl red indicator added. The solution color was brought to amber by adding 0.2N HCl and then 5.0 more cc were added. The cadmium acetate absorbers were filled with a solution containing 100 gm cadmium acetate per litre of H_2O and the

absorption train was connected in the system.

Before the wet-test meter was added to the analytical train, it was necessary to check if the seal in the pump was leaking or not. This was done by pressurizing the system by closing the three-way stopcock and then noting any change in pressure on the manometer. If there was a leak, the adjusting nut on the packing seal was tightened and the system was rechecked for leaks. The use of the wet-test meter eliminated this operation except for an occasional tightening of the nut to allow for the wearing of the packing seal.

After steady-state had been achieved in the reacting system, the flow was switched to the absorption train for two minutes and then back to the sump. In this time or immediately after, the following readings were taken:

1. Rotameter readings: N_2, H_2S, SO_2
2. Temperatures: Fluidized Bed, Reactor Bed, Reactor Wall
3. Barometric pressure
4. Final wet-test reading and temperature in wet-test meter (when appropriate)

The H_2O_2 solution was then analyzed for H_2SO_4 and the run was repeated.

(ii) Analytic Procedures

After the absorption train had been disconnected from the equipment, an air line was connected to it, and the H_2O_2 solution was stripped of any dissolved H_2S by the air passing through it. This was necessary to prevent a hazy indistinct endpoint during the

titration of H_2SO_4. After 10 minutes, the H_2O_2 solution was titrated with standard NaOH solution, which had been standardized with oxalic acid using a phenolthalein indicator. Since the H_2S analysis was low when there was an H_2O_2 absorber before the cadmium acetate absorber, the H_2S analysis was not performed.

In calibrating the rotameters by chemical analysis, the same procedure as discussed above was used for SO_2. For H_2S, the procedure was as follows: The H_2S was absorbed in cadmium acetate solution. The absorber solutions were poured into a glass-stoppered bottle and the absorber containers were rinsed and this rinse solution was added to the bottle. Five cc of starch indicator solution was added to the CdS solution and then concentrated HCl was added to acidify the solution. The solution was titrated with standard iodine solution, prepared according to Kolthoff and Sandell (34), to a starch endpoint. The iodine solution was standardized against As_2O_3 using the procedure given by Kolthoff and Sandell (35).

The following equations were used in the analytic procedures.

1. NaOH Standardization

$$NaOH + H_2C_2O_4 \cdot 2H_2O \longrightarrow Na_2C_2O_4 + 4H_2O$$

$$\text{Normality NaOH} = \frac{\text{wt. of oxalic acid dihydrate}}{\text{mole wt. of oxalic acid dihydrate}} \times \frac{2}{\text{mls NaOH}} \times 1000$$

2. SO_2 Determination

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

$$\text{Wt. } SO_2\text{(gms)} = \text{mls NaOH} \times \text{normality NaOH} \times .064$$

3. Iodine Standardization

$$As_2O_3 + 2I_2 + 5H_2O \rightleftarrows 2HAsO_4^{=} + 4I^- + 8H^+ \qquad pH = 8$$

Normality Iodine solution = $\frac{\text{wt. } As_2O_3}{\text{mls Iodine}} \quad \frac{1}{.04946}$

4. H_2S Determination

$$H_2S + I_2 \longrightarrow S + 2H^+ + 2I^-$$

Wt. H_2S(gm) = .017 x mls Iodine x normality Iodine

IV. EXPERIMENTAL RESULTS

Four basic types of experimental runs were carried out. The first series ascertained whether there was any reaction occurring between H_2S and SO_2 in the reaction system in the absence of the Porocel catalyst. The second series was designed to investigate whether passing H_2S through the H_2O_2 absorber solution and then absorbing it in the cadmium acetate solution had any effect on the reliability of the H_2S analysis. The possibility of the H_2S reacting in the presence of the Porocel catalyst was studied in a third set of runs. The final series of runs investigated the kinetics of the reaction of H_2S within the presence of the Porocel catalyst.

The results in Table 1 for runs 1 and 2 show that while the SO_2 analysis indicates that there is no reaction occurring, the H_2S analysis does not confirm this observation. Run 3 was conducted to see if a satisfactory H_2S determination could be obtained by removing H_2O_2 absorber and not having any SO_2 in the gas stream. It was found that the H_2S determination under these conditions indicated that no reaction was occurring.

The effect of H_2O_2 absorber on the H_2S analysis is shown in Table 2. Approximately 25 mls of 0.15N H_2SO_4 were added to the H_2O_2 absorber to simulate the SO_2 which on absorption would have been converted to H_2SO_4. A mixture of N_2-H_2S was then passed through the reactor and analyzed for H_2S. The amount of H_2S leaving the reactor was found to be 92 to 95% of that entering. Because these runs in Table 2 had been conducted after the Porocel catalyst had been added

to the reactor, it was necessary to conduct the runs shown in Table 3 to check on the possible decomposition of H_2S in the presence of the Porocel catalyst. These runs indicate that between 0.5 to 2.0% of H_2S is decomposing under the conditions of 760 mm Hg pressure and 453 degrees F. The results from Table 3 when applied to those of Table 2 would indicate that the determination of H_2S after passing the gas stream through an H_2O_2 absorber is not satisfactory.

The rates of reaction of H_2S with SO_2 in the presence of a Porocel catalyst at 760 mm Hg pressure and 453 degrees F are shown in Table 4. The raw experimental data for these runs is shown in the Appendix on page 54. The following relationships were used in preparing Table 4:

$$\text{Wt. of } H_2S \text{ converted} = \text{Wt. of } SO_2 \text{ converted} \times 2 \times \frac{\text{Mole Wt. of } H_2S}{\text{Mole Wt. of } SO_2}$$

$$H_2S \text{ Conversion} = \frac{\text{Wt. of } H_2S \text{ converted}}{\text{Wt. of } H_2S \text{ in feed}}$$

The exit compositions were calculated using the following relationships:

$$\text{Moles of } H_2O \text{ formed} = \text{Moles of } H_2S \text{ converted}$$

$$\text{Moles of Sulfur vapor} = \frac{\text{Wt. of } H_2S \text{ converted}}{\text{Average Mole Wt. of Sulfur vapor}^{*}} \times \frac{3}{2} \times \frac{\text{Mole Wt. of Sulfur}}{\text{Mole Wt. of } H_2S}$$

The H_2S composition of the exit gas stream was not corrected for the H_2S decomposition shown in Table 3.

*See Appendix page 65 for this calculation.

TABLE 1

CATALYTIC ACTIVITY OF REACTOR WALLS

Run No.	Flow Rate In gm/min			Flow Rate Out gm/min			Temperature Degrees F			Material Recovery*	
	N_2	H_2S	SO_2	N_2	H_2S	SO_2	Reactor Bed	Reactor Wall	Fluidized Bed	H_2S	SO_2
1	2.06	0.237	0.221	2.06	0.2265	0.221	527	528	530	95.6	100
2	2.29	0.306	0.223	2.29	0.298	0.222	466	462	464	92.3	99.6
3**	2.29	0.296	0	2.29	0.296	0	466	462	464	100	-

No Porocel catalyst added.

Pressure = 760 mm Hg.

*Defined as Material Recovery = $\frac{\text{Flow out of component (determined by analysis)}}{\text{Flow in of component}}$

**Run 3 conducted with no SO_2 entering and with H_2O_2 absorber removed.

TABLE 2

EFFECT OF H_2O_2 ABSORBER ON H_2S ANALYSIS

Run No.	Flow Rate In gm/min		Flow Rate Out gm/min		Temperature Degrees F			H_2S Ratio*
	N_2	H_2S	N_2	H_2S	Reactor Bed	Reactor Wall	Fluidized Bed	
1	1.90	0.2050	1.90	0.1905	452	455	456	95.1
2	1.90	0.1350	1.90	0.1253	455	455.5	455	92.6
3	1.90	0.2250	1.90	0.2040	450	453	453	91.95

Catalyst charge = 0.5226 gm of Porocel

Pressure = 760 mm Hg

*H_2S Ratio = $\frac{H_2S \text{ flow out (determined by analysis)}}{H_2S \text{ flow in}}$

TABLE 3

REACTION OF HYDROGEN SULPHIDE IN THE

PRESENCE OF POROCEL CATALYST

Run	Flow In gm/min		Flow Out gm/min		Temperature Degrees F			Material
No.	N_2	H_2S	N_2	H_2S	Reactor Bed	Reactor Wall	Fluidized Bed	Recovery of H_2S
1	1.90	0.1880	1.90	0.1868	451.5	453	455	99.5
2	1.90	0.1940	1.90	0.1900	451	452	453	97.9
3	1.90	0.2450	1.90	0.2400	453	453	453	98.0
4	1.90	0.2250	1.90	0.2215	451.5	453	455	98.5

Weight of catalyst = .5227 grams of Porocel

Pressure = 760 mm Hg

H_2O_2 absorber removed from the absorption train

TABLE 4

EXPERIMENTAL RATES OF REACTION OF H_2S WITH SO_2

Run No.	Rate x 10^2 $\frac{\text{gm mole } H_2S \text{ reacted}}{\text{hr gm catalyst}}$	P_{H_2S} x 10^2* atm	P_{SO_2} x 10^2 atm	Temperature Degrees F
1	4.96	2.99	1.50	453
2	3.49	2.20	1.10	453
3	4.59	2.71	1.39	453
4	6.26	3.43	1.70	453
5	6.72	4.23	2.10	453
6	6.22	3.87	1.96	455
7	9.75	4.88	2.43	453
8	7.60	4.66	2.35	451
9	9.70	4.89	2.44	453
10	10.14	5.38	2.68	454
11	14.90	5.95	2.92	453
12	16.10	6.33	3.11	453
13	12.68	5.75	2.87	453

Catalyst weight = 0.5227 gm of Porocel

Pressure = 760 mm Hg

* P_{H_2S} was not corrected for amount of H_2S reacted by decomposition.

V. DISCUSSION

(i) H_2S Decomposition

The experimental results shown in Table 3 indicated that H_2S is decomposing under the test conditions. Approximately 0.5 to 2.0% of the H_2S was found to be unaccounted for after passing the N_2-H_2S mixture over the catalyst at temperatures between 451 degrees and 453 degrees F. Since the experimental error in chemical analysis is of a similar level as this conversion, not too much significance can be attached to the absolute value of this conversion. These findings are in agreement with Darwent and Roberts (18) who found that H_2S would undergo heterogeneous catalytic decompositions on glass surfaces at temperatures between 27 degrees and 650 degrees C. They determined the amount of H_2 formed, which would seem to be the best way to analyze the reacting system at low conversions.

Other investigators studying the reaction of H_2S with SO_2 did not apparently consider the possibility of H_2S decomposition; however, if chemical analysis were done for H_2S and SO_2, there should be a slightly greater amount of H_2S reacted than that calculated from the amount of SO_2 reacted. An examination of the analytical procedures of the other investigators of the reaction of H_2S with SO_2, discloses the following:

1. Taylor and Wesley (8): Their analytical procedure of complete absorption of H_2S, SO_2 and H_2O in NaOH solution would not show any discrepancy between H_2S and SO_2 conversions.

2. Doumani et al (13): A table of analytic results was given in their paper. They started with a feed stream containing H_2S to SO_2 in a 2:1 ratio, consequently the product stream should be the same ratio of the unreacted amounts of these compounds if H_2S reacts solely with SO_2. For nine reported results, the ratio is less in four cases, equal in two cases, and larger in the remaining three. These results do not seem to indicate any systematic trend.

3. Gamson and Elkins (14): They analyzed for both H_2S and SO_2 but did not include a complete set of analyses in their paper.

4. Herdon and Morningstar (6): They gave operating data for a plant producing sulfur by reacting H_2S with SO_2. The material balance given in their paper indicates that 0.8% more H_2S was reacted than that which would be calculated from the amount of SO2 reacted. This would seem to indicate that H_2S could be undergoing decomposition to a small extent.

5. Hammar (11): In the majority of his runs, he reports only the analysis for H_2O. However, in a limited number of cases, he also reports H_2S and SO_2 analyses. Since the procedure which he used leads to an incorrect determination of H_2S, therefore these results are inconclusive regarding H_2S decomposition.

The importance of the decomposition reaction of H_2S is that if a 2:1 ratio of H_2S to SO_2 is fed to a catalytic converter, an excess of SO_2 will remain because insufficient H_2S is available for the reaction with SO_2.

(ii) Homogeneous Reaction of H_2S with SO_2

The runs conducted without any catalyst in the reactor indicate two things: The homogeneous reaction of H_2S with SO_2 is not significant at the operating condition, and the stainless steel walls of the reactor and recirculation lines do not exhibit any catalytic activity at the operating conditions.

(iii) Reaction Mechanisms

Table 5 gives a summary of the various rate equations which were investigated, the technique employed in checking them with the experimental data, and the results obtained. In the Appendix page 70 the derivations of the various rate equations from their mechanisms are given. Hammar found that mechanism (1) best correlated his data. This is a mechanism based on a trimolecular reaction which occurs between molecular SO_2 and dissociated H_2S both in the adsorbed state with the surface reaction rate controlling. This mechanism did not correlate the data obtained in this work.

Mechanisms (1) and (2) (mechanism (2) is similar to (1) except that it is a bimolecular reaction) were tested with the experimental data using the least squares technique of curve fitting. The computational work was done by the University computer. Because the data were obtained at a constant ratio of P_{H_2S}/P_{SO_2}, it is possible

TABLE 5

TESTED REACTION MECHANISMS

Mechanism No.	Mechanism	Rate Equation *	Test	Results	Agreement
1	Trimolecular surface reaction between molecular SO_2 and dissociated H_2S both adsorbed is rate controlling.	$\frac{\alpha P_1 P_2}{(1 + K_1 P_1^{\frac{1}{2}} + K_2 P_2 + K_3 \ldots_3)^3}$	Least Squares	Least squares fit gives negative H_2S adsorption coefficients.	No
2	Same as 1 except is a bimolecular reaction.	$\frac{\alpha P_1^{\frac{1}{2}} P_2}{(1 + K_1 P_1^{\frac{1}{2}} + K_2 P_2 + K_3 P_3)^2}$	"	"	No
3	Similar to 1 except H_2S does not dissociate on adsorption.	$\frac{\alpha P_1^2 P_2}{(1 + K_1 P_1 + K_2 P_2)^3}$	Linearity	Plot does not give a straight line.	No
4	Similar to 2 except H_2S does not dissociate on adsorption.	$\frac{\alpha P_1 P_2}{(1 + K_1 P_1 + K_2 P_2)^2}$	"	"	No
5	Adsorption step is rate controlling.	$\frac{\alpha P_1}{(1 + K_2 P_2)}$	"	Plot gives a straight line but has negative adsorption coefficients.	No

* See Appendix D, page 70, for derivation.

For mechanisms 1 and 2, $P_1 = P_{H_2S}$, $P_2 = P_{SO_2}$, and $P_3 = \sum VPs_v$, in the other mechanisms there is no specification.

Continued . . .

Mechanism No.	Mechanism	Rate Equation	Test	Results	Agreement
6	Adsorption of one reactant is rate controlling. This reactant is dissociated on a single site.	$\frac{\alpha P_1^{\frac{1}{2}}}{(1 + K_2P_2)}$	Linearity	Plot does not give a straight line.	No
7	Similar to 6 except adsorption occurs on two sites.	$\frac{\alpha P_1}{(1 + K_2P_2)^2}$	"	"	No
8	Reaction between a gas molecule and an adsorbed molecule is rate controlling.	$\frac{\alpha P_1P_2}{(1 + K_2P_2)}$	"	"	No
9	Similar to 8 except that the adsorbed molecule is dissociated.	$\frac{\alpha P_1P_2^{\frac{1}{2}}}{(1 + K_2P_2^{\frac{1}{2}})}$	"	"	No

to check mechanisms (3) to (9) by linearity tests. If the ratio was not constant, the least squares method must be used.

A first criterion in testing a rate expression by means of least squares is that the data must yield positive adsorption coefficients. In the case of mechanisms (1) and (2), the adsorption coefficient for H_2S was found to be negative in each case which would eliminate these mechanisms.

The linearity test is a rapid and easy way of checking the consistency of the data with a given rate equation. The rate equation is algebraically modified to give a linear form. In this method, a plot of partial pressure of one reacting component versus the "linear variable" determined by the form of the expression, should give a straight line if the data agrees with rate expression. The adsorption coefficients again must be positive. Mechanisms (5) and (6) (in both cases the adsorption step is rate controlling in (5) the component whose adsorption is rate controlling does not dissociate on adsorption while in (6) it does) were found to be only mechanisms to give straight line plots. However on further checking, it was found that they contain negative adsorption coefficients. With exception of mechanisms (1) and (2), the remaining mechanisms were checked without considering the effect of products formed during the course of the reaction. This was done because mechanisms (3) to (9) can not be expressed in a linearized form if the product adsorption terms are considered. Neglecting the product adsorption is probably justified since the

conversions were only of the order of 20%. Of the approaches tested, no mechanism was found which was consistent with the experimental data.

(iv) Catalyst Surface Temperature

Using the highest reaction rate from the experimental data, the difference between the gas temperature and the catalyst surface temperature was estimated by the method of Yoshida et al (36). This calculation is given in the Appendix on page 77. The calculation indicated that this method predicted a difference of 0.1 degree C between the two temperatures with recycle pump in operation. With no recycle, the predicted difference was 0.2 degree C. These low differences result from the combined factors of relatively low heat of reaction, not an extremely high rate of reaction per unit weight of catalyst, and the relatively small diameter of the individual catalyst particles used.

(v) Catalyst Activity

All of the experimental data were obtained with one charge of catalyst. The catalyst was initially treated by passing a N_2-H_2S mixture through the reacting system at 453 degrees F and then a N_2-H_2S-SO_2 mixture was circulated through the reaction system. During this time, the analytic techniques were perfected. The possibility of H_2S decomposition and the validity of the analytic methods were investigated. These runs brought the catalyst to a stable level of activity for use in studying the reaction of H_2S with SO_2. When

experimental runs of exit concentrations of H_2S greater than 8% were attempted, the catalyst became deactivated probably by the deposition of sulfur in the catalyst pores. The catalyst activity could not be restored by maintaining the catalyst at 453 degrees F and passing N_2 through the system for three hours. Doumani (13) suggests the activity can be restored by heating to 500 degrees C. Because a teflon seal was used in the recirculation pump, it was not possible to exceed 500 degrees F. This charge of catalyst was then removed and replaced by a fresh charge; however, the previous level of activity of the first charge could not be obtained even after passing N_2-H_2S through the reactor for 6 hours at 453 degrees F. The results obtained on the second charge were scattered and initially the activity was higher than the previous charge. However, in the latter run (after two days of testing), the activity was closely approaching that of the first charge. This indicates that some care must be exercised to ensure that the catalyst charges will have similar activities.

(vi) Leakage

The method of analysis using a wet-test meter to obtain the flow of the inert component N_2 (to determine what portion of the product stream was sampled) is a somewhat satisfactory solution to the problem of leakage, which is almost inherent in recycle systems. However, as can be seen in the Appendix page 63, the additional error arising from the measurement of leakage leads to almost double the percent error in rate of reaction as compared to the case where the total outlet stream was sampled.

VI. CONCLUSIONS

(i) A small fraction of H_2S appears to be decomposing in the presence of the Porocel catalyst.

(ii) No rate expression could be found which would satisfactorily correlate the experimental data obtained in this study.

(iii) Temperature differences between the gas phase and the surface of the catalyst was estimated to be less than 0.1 degree C.

(iv) Care must be exercised in order to have reproducible catalyst activities.

(v) With this system the problem of leakage can be solved by measuring an inert component in the sample stream as well as measuring a component which is reacting.

VII. RECOMMENDATIONS

1. The autocatalytic effect of water vapor reported by Murthy and Rao (10) could be investigated by adding water vapor to the inlet feed stream. The reaction rate as a function of water concentration could then be studied.

2. The analytical method used for SO_2 determination is satisfactory; however, a method of analyzing for H_2S before the H_2O_2 absorber should be used. The method used by Smith (19) might be suitable.

3. In further investigation of the reaction of H_2S in the presence of Porocel catalyst, it would be desirable to analyze for the reaction products rather than the reactants since the conversion level is low.

4. The experimental results obtained are thought to be good but because they are limited in number more data must be obtained before too many positive conclusions can be drawn. The data presented was obtained on one charge of Porocel catalyst. An attempt was made to use another charge of catalyst; however, the activities of the two charges were different to some extent. A subsequent program should pay close attention to this factor.

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A P P E N D I X A

EXPERIMENTAL AND CALCULATED DATA

TABLE 6

EXPERIMENTAL DATA

Run	Rotameter Readings			Temperatures Degrees F*			Outlet Sample N_2				SO_2
No.	N_2	H_2S	SO_2	1	2	3	Time Sec.	Vol. ft^3	Pressure mm Hg	Temperature Degrees F	Titration mls NaOH**
1	4.20	4.75	4.85	453	444	444	30	Total	-	-	12.15
2	4.20	3.00	3.60	453	445	445	30	Total	-	-	8.85
3	2.30	2.50	2.75	453	448	450	30	Total	-	-	6.37
4	2.30	3.00	3.55	453	446	451	30	Total	-	-	7.92
5	2.30	3.25	4.00	453	449	451	30	Total	-	-	9.14
6	2.30	3.50	4.35	455	451	452	30	Total	-	-	10.00
7	2.30	4.00	5.18	453	447	449	30	Total	-	-	11.65
8	2.30	3.70	4.80	451	-	-	60	.0486	701	74	17.10
9	2.30	4.00	5.17	453	450	453	120	.0702	687	75	25.54
10	2.30	4.26	5.67	454	450	452	120	.0860	695	68	35.55
11	2.28	4.79	6.55	453	448	450	120	.0999	701	74.5	45.54
12	2.30	5.10	7.05	453	447	450	120	.0774	699	74.5	37.66
13	2.47	4.75	6.55	453	449	451	120	.1025	701	74.5	45.34

Weight of catalyst = 0.5227 gm of Porocel

Reactor pressure = 760 mm Hg

* 1 = Reactor bed, 2 = Reactor wall, 3 = Fluidized Bed

** Normality of NaOh solution = 0.155 N

TABLE 7

CALCULATED DATA

Run No.	Inlet Comp. %			Amount of SO_2 Converted gm/min	Ave. Molecular Weight of Sulfur Vapor	Outlet Comp. %					Rate gm moles H_2S reacted gm hr x 10^2
	N_2	H_2S	SO_2			N_2	H_2S	SO_2	H_2O	S_x	
1	95.00	3.335	1.665	0.0138	223.6	95.10	2.99	1.50	0.34	0.07	4.96
2	96.33	2.445	1.225	0.0097	223.1	96.40	2.20	1.10	0.25	0.05	3.49
3	95.08	3.26	1.665	0.01275	226.6	95.21	2.71	1.39	0.57	0.12	4.59
4	93.73	4.19	2.08	0.01745	227.8	93.95	3.43	1.70	0.76	0.16	6.26
5	93.07	4.61	2.32	0.0187	227.7	93.27	3.87	1.96	0.75	0.16	6.22
6	92.47	5.02	2.51	0.0234	228.2	92.70	4.23	2.10	0.80	0.17	6.72
7	91.00	6.00	3.00	0.0272	229.6	91.31	4.88	2.43	1.14	0.24	9.75
8	91.79	5.42	2.79	0.0230	228.2	91.91	4.66	2.35	0.89	0.17	7.60
9	91.00	6.00	3.00	0.0280	229.6	91.29	4.89	2.44	1.14	0.24	9.70
10	90.19	6.54	3.27	0.0310	229.7	90.53	5.38	2.68	1.17	0.24	10.14
11	88.53	7.68	3.79	0.0435	231.5	89.07	5.95	2.92	1.71	0.35	14.90
12	87.87	8.12	4.01	0.0465	232.2	88.34	6.33	3.11	1.84	0.38	16.10
13	89.38	7.08	3.54	0.0373	231.0	89.73	5.75	2.87	1.37	0.28	12.68

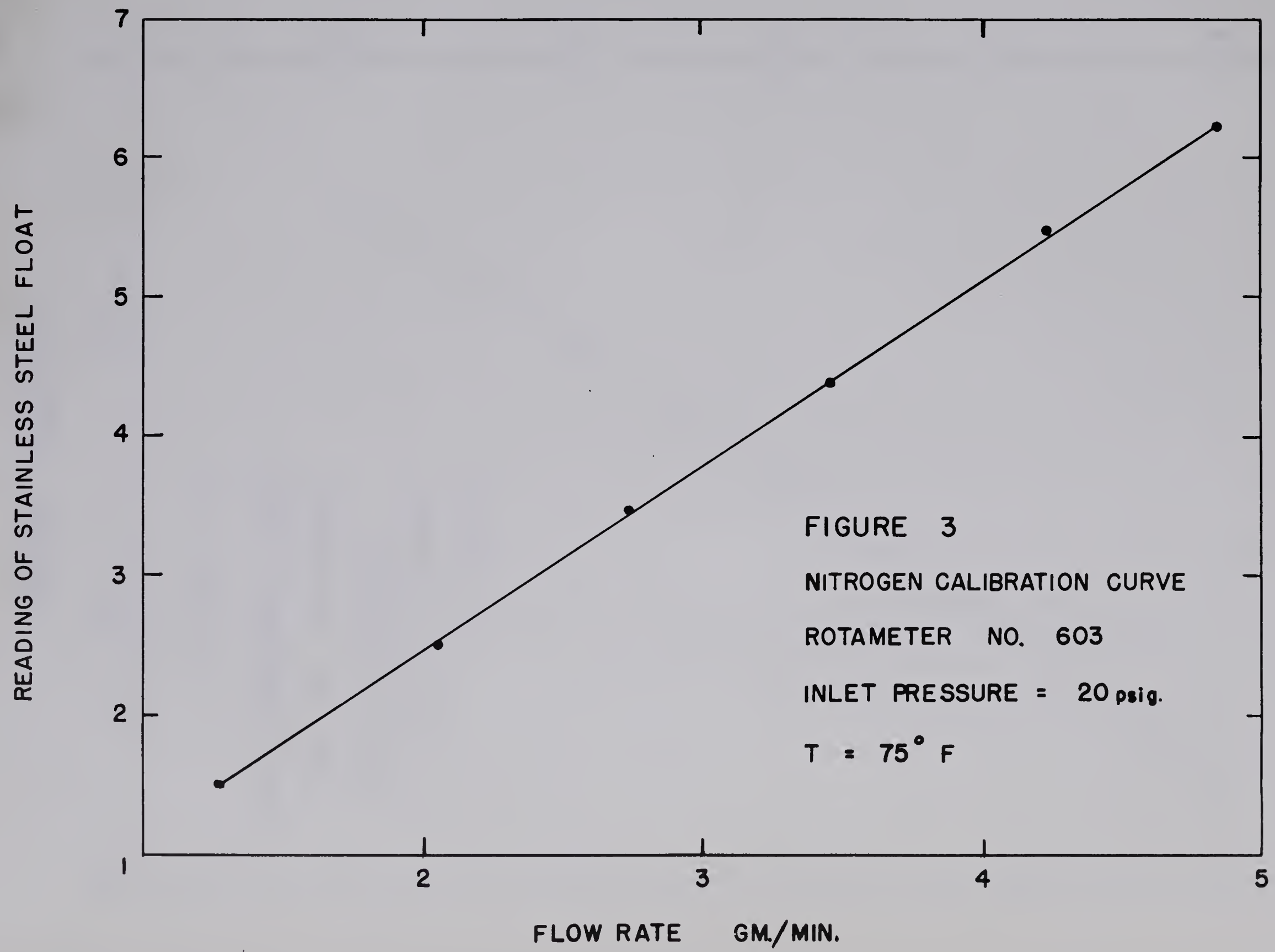
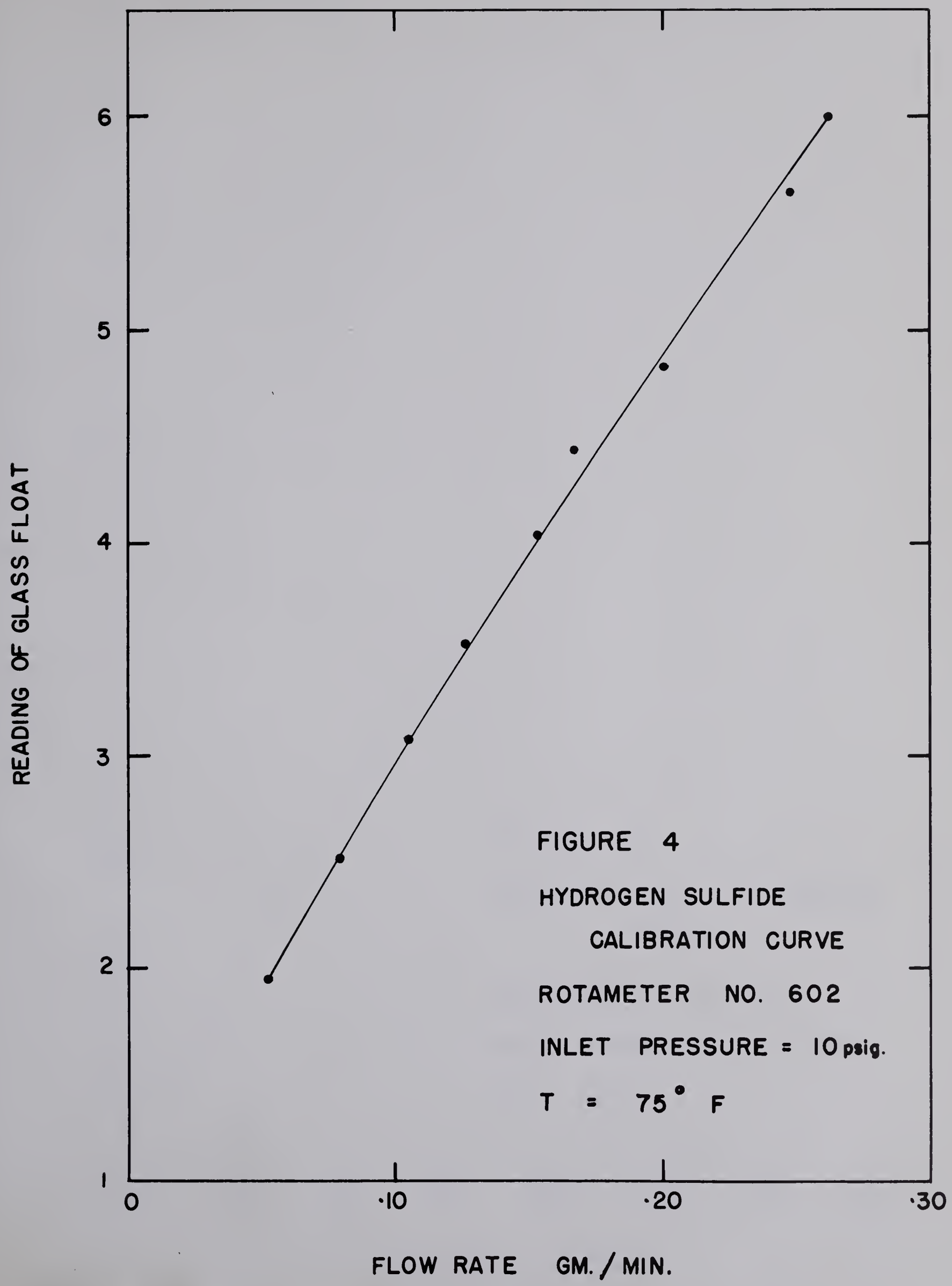

READING OF STAINLESS STEEL FLOAT
7
6
5
4
3
2
1
2
3
4
5
FLOW RATE GM./MIN.
NITROGEN CALIBRATION CURVE
ROTAMETER NO. 603
INLET PRESSURE = 20 psig.
T = 75° F

FIGURE 3


READING OF GLASS FLOAT
6
5
4
3
2
1
0
·10
·20
·30
FLOW RATE GM. / MIN.
FIGURE 4
HYDROGEN SULFIDE
CALIBRATION CURVE
ROTAMETER NO. 602
INLET PRESSURE = 10 psig.
T = 75° F

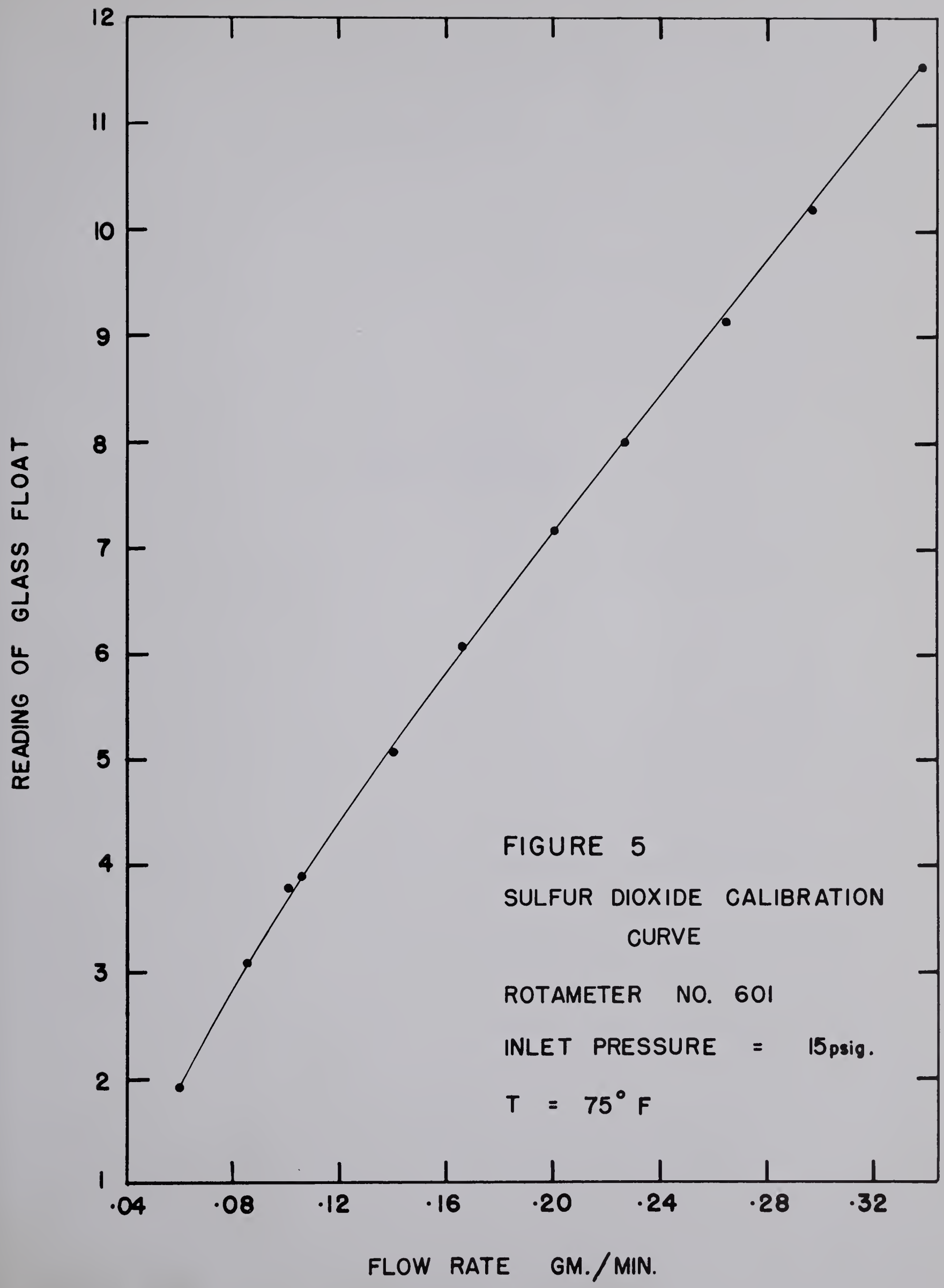


FIGURE 5

SULFUR DIOXIDE CALIBRATION CURVE

A P P E N D I X B

SAMPLE CALCULATION

The sample calculation will be performed on the data from Run No. 8.

DATA: Reactor temperature = 451 degrees F

Reactor pressure = 760 mm Hg

Wt. of catalyst = 0.5227 gm

Inlet:

Component	Rotameter Reading
N_2	2.30
H_2S	3.70
SO_2	4.80

Outlet: N_2 sample: .0486 ft^3 at 701 mm Hg and 74 degrees F for 60 sec.

SO_2 sample: 17.10 mls of 0.155 N NaOH titrated from 60 sec. sample

Calculation

The inlet flows of the components can be calculated using their respective calibration curves shown in Figures 3, 4 and 5.

Inlet:

Component	Rotameter Reading	Flow Rate (gm/min)	Composition (mole %)
N_2	2.30	1.90	91.79
H_2S	3.70	0.1360	5.42
SO_2	4.80	0.1320	2.79

The portion of the total outlet flow which was sampled can be determined by the amount of N_2 in the outlet sample.

$$\text{Weight of } N_2/\text{min} = 0.0486 \left(\frac{28.3}{22.4}\right)\left(\frac{273}{297}\right)\left(\frac{701}{760}\right) 28 = 1.456 \text{ gm/min}$$

$$\text{Fraction of outlet flow sampled} = \frac{1.456}{1.90} = 0.766$$

$$\text{Weight of } SO_2 \text{ in outlet sample/min} = \frac{17.10}{1000}(0.155)(32)$$

$$= 0.0848 \text{ gm/min}$$

$$\text{Total unreacted weight of } SO_2 \text{ in outlet flow/min} = \frac{0.0848}{0.766}$$

$$= 0.1108 \text{ gm/min}$$

$$\text{Amount of } SO_2 \text{ reacted/min} = 0.1320 - 0.1108 = 0.0212 \text{ gm/min}$$

$$\text{Equivalent weight of } H_2S \text{ reacted/min} = 0.0212 \left(\frac{68}{64}\right) = 0.0225 \text{ gm/min}$$

$$\text{Weight of sulfur formed/min} = 0.0225 \left(\frac{96}{68}\right) = 0.0318 \text{ gm/min}$$

$$\text{Weight of } H_2O \text{ formed/min} = 0.0225 \left(\frac{18}{34}\right) = 0.01192 \text{ gm/min}$$

In order to calculate the exit composition, it is necessary to calculate the average molecular weight of the vapor phase sulfur. The calculation of the composition of the sulfur vapor is shown in Appendix C. The pressure of S_8 has been determined as a function of $x_{H_2S}(P_{H_2S})_{Feed}$. From this, pressures of S_6 and S_2 can be calculated from their thermodynamic equilibrium relationships with S_8.

$$x_{H_2S} = \frac{\text{weight of } H_2S \text{ converted/min}}{\text{feed rate of } H_2S\text{/min}} = \frac{0.0225}{0.1360} = 0.165$$

$$x_{H_2S}(P_{H_2S})_F = 0.165\ (1)\ 0.0542 = 0.00090 \text{ atm}$$

From Figure 6 in Appendix C

$$P_{S_8} = 0.00100 \text{ atm}$$

At this temperature

$$P_{S_6}^4 / P_{S_8}^3 = 3 \times 10^{-4}$$

$$P_{S_2}^4 / P_{S_8} = 1 \times 10^{-18}$$

$$P_{S_6} = 7.40 \times 10^{-4} \text{ atm}$$

$$P_{S_2} = 5.62 \times 10^{-6}$$

The total vapor pressure of the various sulfur species is

$$17.46 \times 10^{-4} \text{ atm.}$$

The composition of sulfur vapor is:

Component	Mole %
S_8	57.30
S_6	42.40
S_2	0.30

Average molecular weight of sulfur vapor

$$= 0.5730(32)8 + 0.4240(32)6 + 0.0030(32)2$$

$$= 228.2$$

The exit composition is:

Component	Weight Rate of Flow (gm/min)	Molecular Rate of Flow (gm mole/min)	Mole %
N_2	1.900	0.06786	91.91
H_2S	0.1135	0.00344	4.66
SO_2	0.1108	0.00173	2.35
Sulfur vapor	0.0318	0.00014	0.19
H_2O	0.01192	0.00066	0.89

Total flow rate = 0.07383 moles/min

$$\text{Rate of reaction} = \frac{0.0225}{34.08}\left(\frac{60.0}{0.5227}\right) = 7.6 \times 10^{-2}\ \frac{\text{gm moles } H_2S \text{ reacted}}{\text{hr gm catalyst}}$$

ESTIMATION OF ERRORS

The reaction rate is directly proportional to the amount of SO_2 reacted. The determination of the amount of SO_2 reacted is subject to the following errors:

1. Rotameter readings

A rotameter can be read to ±0.025 units of the scale. Using the calibration curves for each component, the corresponding percent error at the flow rates used in the previous sample calculation can be determined.

N_2	±0.79%
H_2S	±0.55%
SO_2	±0.76%

2. N_2 sample

It is dependent upon the volume, pressure, temperature and time measurements.

0.0486 ft^3 ± 0.002 ft^3	=	0.0486 ft^3 ± 0.41%
701 mm Hg ± 1 mm Hg	=	701 mm Hg ± 0.14%
534°R ± 0.5°R	=	534°R ± 0.09%
60.0 sec ± 0.1 sec	=	60.0 sec ± 0.17%
		± 0.81%

3. SO_2 sample

It is dependent upon the time measurement, the normality of NaOH solution and the volume of NaOH titrated.

$$17.10 \text{ mls} \pm 0.05 \text{ mls} = 17.10 \text{ mls} \pm 0.29\%$$

$$0.155\text{N} \pm 0.001\text{N} = 0.155\text{N} \pm 0.65\%$$

$$60.0 \text{ sec} \pm 0.1 \text{ sec} = 60.0 \text{ sec} \pm \underline{0.17\%}$$

$$\pm 1.11\%$$

The outlet flow of SO_2 has a percent of

$$= \pm (0.79\% + 0.81\% + 1.11\%)$$

$$= \pm 2.71\%$$

The percent error in the amount of SO_2 reacted is:

$$0.1320 \text{ gm} \pm 0.76\% = 0.1320 \text{ gm} \pm 0.0010 \text{ gm}$$

$$- 0.1108 \text{ gm} \pm 2.71\% = \underline{-0.1108 \text{ gm} \pm 0.0030 \text{ gm}}$$

$$0.0212 \text{ gm} \pm 0.0040 \text{ gm}$$

$$0.0212 \text{ gm} \pm 0.0040 \text{ gm} = 0.0212 \text{ gm} \pm 18.9\%$$

If all the outlet stream was sampled that is no leakage, the percent error in the determination of SO_2 reacted would be:

$$0.1320 \text{ gm} \pm 0.76\% = 0.1320 \text{ gm} \pm 0.0010 \text{ gm}$$

$$- 0.1108 \text{ gm} \pm 1.11\% = \underline{- 0.1108 \text{ gm} \pm 0.0012 \text{ gm}}$$

$$0.0212 \text{ gm} \pm 0.0022 \text{ gm}$$

$$0.0212 \text{ gm} \pm 0.0022 \text{ gm} = 0.0212 \text{ gm} \pm 10.4\%$$

The percent error of the amount of SO_2 reacted is the same as the percent error in reaction rate since the percent error in the catalyst weight is insignificant compared with the SO_2 error.

A P P E N D I X C

CALCULATION OF SULFUR VAPOR COMPOSITION

The sulfur vapor composition was calculated using the procedure of Hammar (1) and the data of Kelley (2). Hammar calculated the sulfur vapor composition for a given conversion of H_2S and inlet pressure of H_2S by selecting a value of Ps_8, Ps_6 and Ps_2 were then calculated from the equilibrium data of Kelley for equations (1) and (2).

$$S_{8\ g} = 4S_{2\ g} \qquad (1)$$

$$\Delta F_1^\circ = 95,200 - 13.8\ T \log T - 16.28\ T \text{ calories}$$

$$3S_{8\ g} = 4S_{6\ g} \qquad (2)$$

$$\Delta F_2^\circ = 29,250 - 4.6\ T \log T - 27.81\ T \text{ calories}$$

The conversion is then by definition equal to:

$$X_{H_2S} = \frac{\sum VPsv}{1.5\ (P_{H_2S})_F}$$

where X_{H_2S} = fractional conversion of H_2S

Psv = partial pressure of V sulfur

$(P_{H_2S})_F$ = partial pressure of H_2S in feed stream

Sample calculation

$$T = 505\ K$$

$$\Delta F_1^\circ = 41,560 \text{ calories}$$

$$\Delta F_2^\circ = 8,850 \text{ calories}$$

$$\Delta F^\circ = RT \ln K$$

$$K = 1 \times 10^{-18}$$

$$K_2 = 3 \times 10^{-4}$$

---

(1) Hammar, B.C.G., Doktorsavhandal. Chalmers Tek. Hogskola, No. 14, 166 pp (1957) (in English)

(2) Kelley, K.K., U.S. Bur. of Mines Bull. 406 (1937)

Assume $Ps_8 = 0.001$ atm

$$Ps_2^4 / Ps_8 = 1 \times 10^{-18} = Ps_2^4 / 1 \times 10^{-3}$$

$$Ps_2 = 5.63 \times 10^{-6} \text{ atm}$$

$$Ps_6^4 / Ps_8^3 = 3 \times 10^{-4} = Ps_6^4 / (1 \times 10^{-3})^3$$

$$Ps_6 = 7.4 \times 10^{-4}$$

$$\Sigma VPsv = 1 \times 10^{-3}(8) + 7.4 \times 10^{-4}(6) + 5.63 \times 10^{-6}(2)$$

$$= 0.01245 \text{ atm}$$

$$x_{H_2S}(P_{H_2S})_F = \frac{0.01245}{1.5} = 0.00830 \text{ atm}$$

TABLE 8

SULFUR VAPOR COMPOSITION WITH VARYING CONVERSION AND VARYING INLET H_2S PRESSURE

Ps_8 atm	$x_{H_2S}(P_{H_2S})_{Feed}$ atm	$\sum VPs_v$ atm
0.00025	0.00239	0.003580
0.0005	0.00412	0.006193
0.0010	0.00830	0.01245
0.0015	0.01202	0.01803
0.0020	0.01568	0.02348
0.0025	0.01924	0.02883
0.0030	0.02275	0.03411
0.0040	0.02980	0.04456
0.0050	0.03660	0.05492

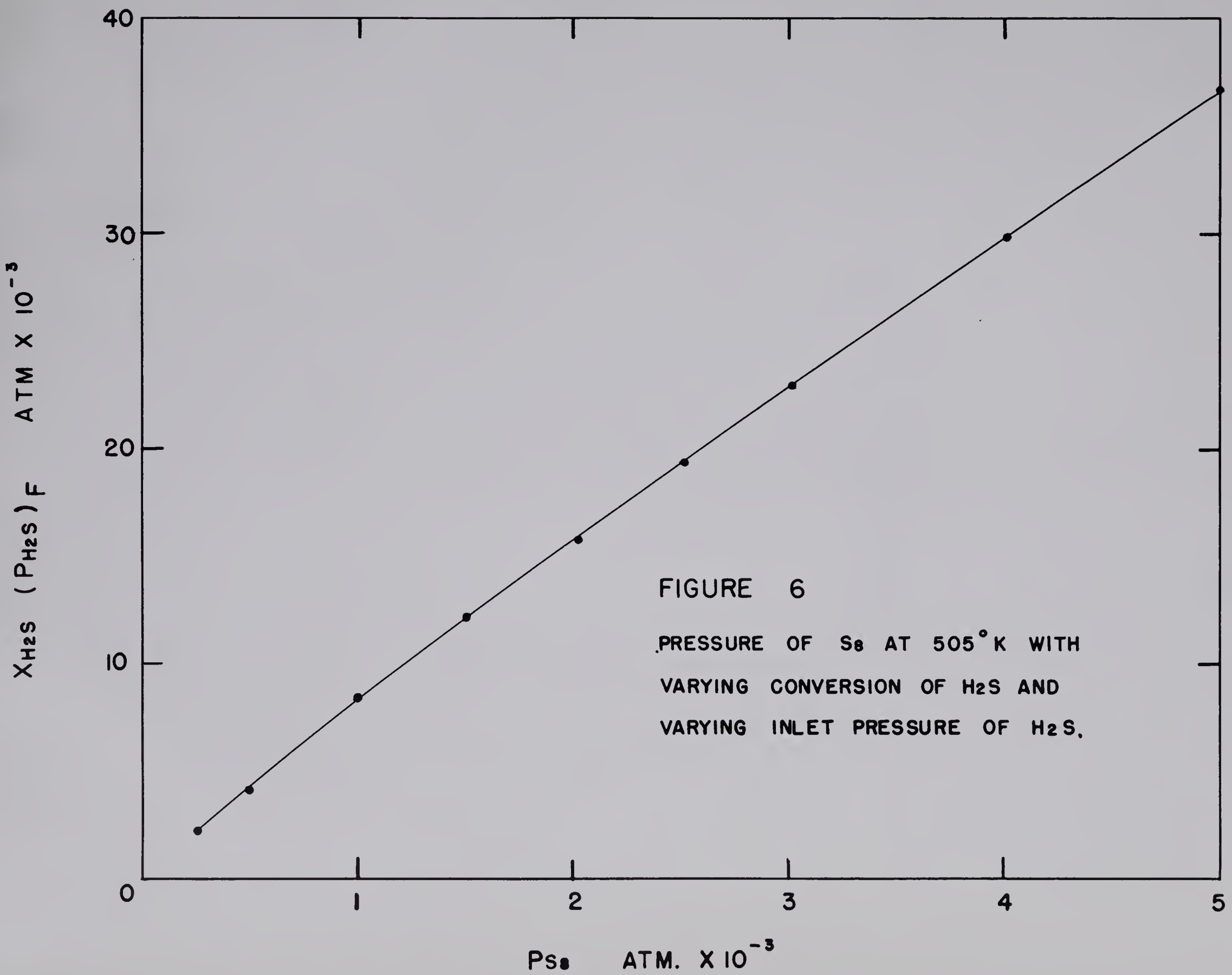


FIGURE 6

PRESSURE OF S_8 AT 505°K WITH VARYING CONVERSION OF H_2S AND VARYING INLET PRESSURE OF H_2S.

A P P E N D I X D

DERIVATION OF REACTION MECHANISMS

Reference: Emmett, P.H., ed., "Catalysis", Reinhold, New York, 1954, Vol. 1, pp 75-188

The following nomenclature will be used in the subsequent derivations. Consider two components A and B, let

Θ_A and Θ_B = fraction of sites on the catalyst surface covered by components A and B.

1. Surface reaction between adsorbed molecules is rate controlling.

a.) Reaction between molecular SO_2 and dissociated H_2S both in the adsorbed state. Let component A be the dissociated component. The adsorption of component B can be derived as follows:

$$B + S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} S - B$$

$$v_3 = k_3 P_B (1 - \Theta_A - \Theta_B)$$

$$v_{-3} = k_{-3} \Theta_B$$

where v_3 and v_{-3} = velocity of the adsorption desorption reactions respectively.

k_3 and k_{-3} = rate constants of the reactions

$(1 - \Theta_A - \Theta_B)$ = fraction of sites on which neither A nor B is adsorbed

S = site for adsorption

P_B = partial pressure of B

By equilibrium considerations

$$v_3 = v_{-3}$$

then $k_3 P_B (1 - \Theta_A - \Theta_B) = k_{-3} \Theta_B$ (1)

The dissociation on adsorption can be represented via two routes. For the sake of simplicity in nomenclature, consider the component A as being a symmetrical molecule A_2. This does not have any effect on the derivation except making the nomenclature easier.

(i) Interaction occurs between half of a gas molecule and a single site.

$$1/2\ A_2 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S - A$$

$$v_1 = k_1\ P_{A_2}^{\frac{1}{2}}(1 - \theta_A - \theta_B)$$

$$v_{-1} = k_{-1}\ \theta_A$$

By equilibrium considerations

$$k_1\ P_A^{\frac{1}{2}}(1 - \theta_A - \theta_B) = k_{-1}\ \theta_A \qquad (2)$$

(ii) Interaction occurs between a gas molecule and two sites.

$$A_2 + 2S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2S - A$$

$$v_2 = k_2 P_{A_2}(1 - \theta_A - \theta_B)^2$$

$$v_{-2} = k_{-2}\ \theta_A{}^2$$

By equilibrium considerations

$$k_2 P_{A_2}(1 - \theta_A - \theta_B)^2 = k_{-2}\ \theta_A{}^2 \qquad (3)$$

The solution of (1) and (2) for θ_A and θ_B gives

$$\theta_A = \frac{K_3 P_{A_2}^{\frac{1}{2}}}{(1 + K_3 P_{A_2}^{\frac{1}{2}} + K_1 P_B)}$$

$$\theta_B = \frac{K_1 P_B}{(1 + K_3 P_{A_2}^{\frac{1}{2}} + K_1 P_B)}$$

Similarly the solution of (1) and (3) for θ_A and θ_B gives the same as for (1) and (2); that is, the adsorption isotherms are of the same form. In subsequent work, A will be substituted for A_2.

Mechanism 1

Trimolecular surface reaction between adsorbed dissociated H_2S and adsorbed SO_2 is rate controlling.

$$\text{rate} = \frac{\alpha P_A P_B}{(1 + K_1 P_A^{\frac{1}{2}} + K_2 P_B)^3}$$

Emmett * mentions that surface reactions higher than bimolecular are not known, thus it would seem that there is not much likelihood of this reaction occurring.

Mechanism 2

Similar to Mechanism 1 except that it is a bimolecular reaction.

$$\text{rate} = \frac{\alpha P_A^{\frac{1}{2}} P_B}{(1 + K_1 P_A^{\frac{1}{2}} + K_2 P_B)^2}$$

b.) Reaction between SO_2 and H_2S both in adsorbed state. In this case adsorption isotherms for A and B are the same form as equation (1). The solution of these equations gives:

$$\theta_A = \frac{K_1 P_A}{(1 + K_1 P_A + K_2 P_B)}$$

$$\theta_B = \frac{K_2 P_B}{(1 + K_1 P_A + K_2 P_B)}$$

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* Emmett, P.H., ed., "Catalysis", Reinhold, New York, Vol. 1, p. 130.

Mechanism 3

Trimolecular surface reaction between adsorbed H_2S and SO_2 is rate controlling.

$$\text{rate} = \frac{\alpha P_A^2 P_B}{(1 + K_1 P_A + K_2 P_B)^3}$$

Mechanism 4

Similar to Mechanism 3 except it is a bimolecular reaction.

$$\text{rate} = \frac{\alpha P_A P_B}{(1 + K_1 P_A + K_2 P_B)^2}$$

2. Adsorption of one component is rate controlling.

a.) The component whose adsorption is rate controlling does not dissociate on adsorption. Let A = component whose adsorption is rate controlling. In this case Θ_A is likely quite small and can be neglected. Then

$$\frac{\Theta_B}{1 - \Theta_B} = K_2 P_B$$

$$\text{rate} = k_1 P_A (1 - \Theta_B)$$

Mechanism 5

Adsorption of component which does not dissociate is rate controlling.

$$\text{rate} = \frac{k_1 P_A}{1 + K_2 P_B}$$

b.) Adsorption of component which is adsorbed according to the scheme of half of the gas molecule and a single site. Let A be this component

$$\frac{\Theta_B}{1 - \Theta_B} = K_2 P_B$$

$$\text{rate} = k_1 P_A^{\frac{1}{2}} (1 - \Theta_B)$$

Mechanism 6

Adsorption is rate controlling, adsorption is of half a gas molecule on a single site.

$$\text{rate} = \frac{k_1 P_A^{\frac{1}{2}}}{1 + K_2 P_B}$$

c.) Similar to mechanism 6 except adsorption is a gas molecule on two sites.

$$\frac{\Theta_B}{1 - \Theta_B} = K_2 P_B$$

$$\text{rate} = k_1 P_A (1 - \Theta_B)^2$$

Mechanism 7

Adsorption is rate controlling. Adsorption is that of a gas molecule on two sites.

$$\text{rate} = \frac{k_1 P_A}{(1 + K_2 P_B)^2}$$

3. Reaction between a gas-phase molecule and an absorbed molecule is rate controlling.

a.) Adsorbed molecule is not dissociated. Let B represent this component. Consider that A is small, then

$$\frac{\Theta_B}{1 - \Theta_B} = K_2 P_B$$

$$\text{rate} = k_1 P_A \Theta_B$$

Mechanism 8

Rate controlling step is the reaction between a gas-phase molecule and an adsorbed molecule which is not dissociated.

$$\text{rate} = \frac{k P_A P_B}{1 + K_2 P_B}$$

b.) Adsorbed component is dissociated. Let B represent this component. Θ_A can be neglected since it is small.

$$\frac{\Theta_B}{1 - \Theta_B} = K_2 P_B^{\frac{1}{2}}$$

$$\text{rate} = k_1 P_A \Theta_B$$

<u>Mechanism 9</u>

Rate controlling step is the reaction between a gas-phase molecule and an adsorbed molecule which is dissociated.

$$\text{rate} = \frac{\mathcal{L} P_A P_B}{1 + K_2 P_B}$$

A P P E N D I X E

ESTIMATION OF SURFACE TEMPERATURE OF CATALYST

References: 1. Yoshida, F., Ramaswami, D., and Hougen, O.A., A.I. Ch. E. Journal, 8, 5 (1962)

2. Fulton, J.W., and Crosser, O.K., A.I. Ch. E. Journal, 11, 513 (1965)

At steady-state, a heat balance around the catalyst particle is

Heat generated by reaction = Heat removed from particle

$$r_m \Delta H = h_G \, a_m \, \Delta t$$

where, r_m = molal rate of reaction per unit mass $\frac{gm/moles}{hr\ gm}$

ΔH = molal heat of reaction cal/gm moles

h_G = heat transfer coefficient $\frac{cal}{hr\ cm^2\ °C}$

a_m = external surface area of catalyst particles per unit mass cm^2/gm

Δt = temperature difference between catalyst surface and gas temperature °C

Yoshida et al obtained h_G from the relationship developed by Chilton and Colburn[N].

$$j_H = \frac{h_G}{CpG} \frac{(Cp\mu)^{2/3}}{(k)_f}$$

j_H = heat transfer number

Cp = heat capacity per unit mass at constant pressure $\frac{cal}{gm\ °C}$

G = mass velocity of gas based on total cross-section of bed $\frac{gm}{cm^2\ hr}$

[N] Chilton, T.H., and Colburn, A.P., Ind. Eng. Chem., 26, 1183 (1934)

μ = viscosity centipoise

k = thermal conductivity $\frac{cal}{hr\ cm^2\ C}$

f = properties evaluated at temperature of gas film

Yoshida et al then used the following equation to estimate the temperature difference between the catalyst surface and the gas.

$$t = \frac{r_m \Delta H}{a_m\ Cp\ G} \quad (j_H)^{-1}\ (Pr)_f^{2/3}$$

$$t = Q\ j_H^{-1}\ (Pr)_f^{2/3}$$

$$Re = G/a_v \phi \mu$$

where, Re = Reynolds number

a_v = area of particle per unit volume of bed cm^2/cm^3

ϕ = ratio of external surface available for mass transfer to total external surface area

$$a_v = \frac{6(1 - \epsilon)}{SDp}$$

ϵ = porosity of bed

S = sphericity

Dp = average particle diameter cm

By calculating Re, Q, and Pr, a nomograph given by Yoshida et al on page 8 can be used to calculate Δt.

Sample Calculation Run 12

r_m = 16.1×10^{-2} gm moles of H_2S/hr gm of catalyst

Tgas = 507°K

P = 1 atm

ΔH = -14,500 cal/gm mole of H_2S at T = 507°K and S_8 is the sole sulfur vapor species

Recirculation rate = 0.6 ft^3/min

Particle size is = -20 + 30 mesh

$D_{P_{ave}}$ = 0.027 inches = 0.0685 cm

ϵ = 0.5

Particle shape is cubic or flakes (estimated)

S = 0.8

ϕ = 0.86 *

The gas mixture has the following composition: N_2 - 88.34%, H_2S - 6.33%, SO_2 - 3.11%, H_2O - 1.84%, S - 0.38%. The gas mixture is predominantly N_2 so the properties of N_2 will be used in the calculations.

μ = 0.0260 N_2 at 507°K **

Cp = 7.157 cal/gm mole °C N_2 at 507°K ***

Density of catalyst = 55 lb/ft^3 = 0.88 gm/cc

Inside diameter of reactor = 0.625 in

Density of gas by ideal gas law

$$\rho = \frac{PM}{RT}$$

ρ = 0.042 lb/ft^3

G = 346 $gm/hr\ cm^2$

a_v = 54.8 cm^{-1}

Re = 8.45

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* Gamson, B.W., Chem. Eng. Progr., 47, 19 (1951)

** Perry, J.H., ed., "Chemical Engineers' Handbook", McGraw-Hill, New York, 1950, p. 371

*** Smith, J.M., and Van Ness, H.C., "Introduction to Chemical Engineering Thermodynamics", McGraw-Hill, New York, 1959, p. 122

Calculate a_m by assuming a cubic shape for catalyst particles

$$a_m = \frac{6 \quad Dp^2}{Dp^3}$$

$$a_m = 99.5 \text{ cm}^2/\text{gm}$$

$$Q = 0.322$$

$$Pr = 0.685$$

From nomograph $\Delta t = 0.1^\circ C$, consider the case when there is no recycle

$$G = 65.5 \text{ gm/hr cm}^2$$

$$Re = 1.6$$

$$Q = 1.7$$

From nomograph $\Delta t = 0.2^\circ C$, consider the effect of having used a larger size of catalyst particles; e.g., 6 mesh

$$Dp = 0.131 \text{ in} = 0.332 \text{ cm}$$

$$a_v = 11.3 \text{ cm}^{-1}$$

$$a_m = 20.55 \text{ cm}^2/\text{gm}$$

With a recycle stream

$$Re = 41$$

$$Q = 1.56$$

$$\Delta t = .8^\circ C$$

With no recycle stream

$$Re = 7.75$$

$$Q = 8.15$$

$$\Delta t = 2^\circ C$$